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National Dioxin Study Tier 4 Combustion Sources: Sampling Procedures

Radian Corp., Research Triangle Park, NC

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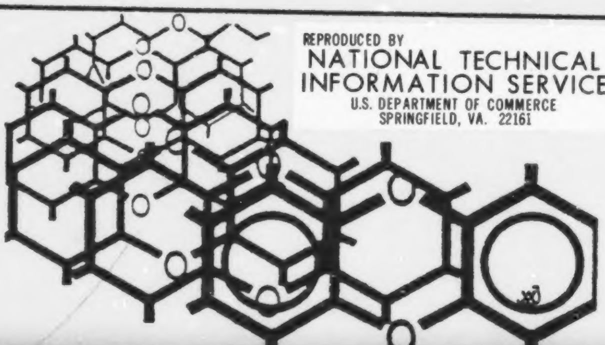
Air

National Dioxin Study Tier 4 — Combustion Sources

Sampling Procedures



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16. ABSTRACT

Tier 4 of the National Dioxin Study has as an objective to determine, by testing, if combustion sources emit significant dioxins to the atmosphere. These tests may be conducted by different test personnel and, in order to keep procedures consistent for all tests, these have been summarized in the form of a sampling procedures manual. Source sampling techniques are described in overview fashion for combustion air, flue gases, liquids, slurries, solids, and sludges.

The sampling procedures address collecting samples for subsequent analysis of dioxins and their precursors. In addition, sampling and analysis techniques are recommended for measuring SO_x, NO_x, CO, CO_2, HCl, O_2, total hydrocarbon, moisture, particulate, molecular weight, and volumetric flow in flue gas streams.

In addition to sampling procedures, the manual presents detailed procedures for site selection, acquisition of design and operating data, safety, and test plan preparation. Quality assurance and control is briefly addressed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
ASME/ASTM/EPA Dioxin Sampling Protocols		Air Pollution Sampling	
Stack Sampling	TCDD		
Combustion Source Sampling	TCDF		
Dioxins	PCDD		
Furans	PCDF		
2,3,7,8-Tetrachlorodibenzo-p-dioxin			
Modified Method 5 with XAD-2			

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National Dioxin Study Tier 4 — Combustion Sources

Sampling Procedures

By
Radian Corporation
Research Triangle, NC 27709

Contract No. 68-02-3513
EPA Project Officer: William H. Lamason

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park, NC 27711

October 1984

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1.0 INTRODUCTION

This document is one component of Tier 4 of the National Dioxin Study. The Tier 4 effort is concerned with combustion sources. The primary objective of the Tier 4 study is to determine if combustion sources emit significant dioxins to the atmosphere. If they do, then the secondary objectives are to quantify these emissions and determine the exposure and risk of living in the proximity of these sources.

This document describes the procedures that will be followed to acquire samples from combustion sources that are sampled as part of the Tier 4 effort. The combustion sources that may be sampled are presented in Table 1-1 and ranked according to their probability of emitting dioxin. Because of the diversity of sources listed and because of the wide variety of sample media (gases, liquids, solids, sludges, and soils) that may be encountered, the exact set of sampling protocols that will be followed at each test cannot be specified at this time. However, the list of approved or applicable protocols for all likely media to be encountered has been developed and is presented in this document.

The purpose of this document is to specify the applicable sampling protocol for each media. These sampling protocols will be used throughout the Tier 4 study. A uniform set of procedures is needed in order to minimize variability introduced by sampling methods. Since many different media will be encountered and a diverse number of sampling locations are available at any combustion source, this document attempts to outline procedures for selection of preferred sampling locations and also outlines preferred sample acquisition methods.

The document does not present or discuss any procedure in sufficient detail to be used as a training manual or step-by-step set of instructions for the following reasons:

1. The sampling methods described are based upon previously developed protocols or methods. Step-by-step instructions for each of these methods can be found in the applicable references.

TABLE 1-1. COMBUSTION SOURCES LISTED IN ORDER OF DECREASING PROBABILITY AS DIOXIN EMISSION SOURCES (NOVEMBER 1984)[1]

Rank A Source Categories
- Sewage Sludge Incinerators
- Black Liquor Boilers

Rank B Source Categories
- Industrial Incinerators
- PCP* Sludge Incinerators
- Carbon Regeneration (industrial)
- Wire Reclamation
- Wood Boilers (firing PCP treated or salt-laden wood)

Rank C Source Categories
- Charcoal Manufacturing
- Wood Stoves
- Mobile Sources
- Small Spreader-stoker Coal Boiler
- Chlorinated Organic Waste Incinerators
- Lime-Cement Kilns Cofired with Chlorinated Organic Wastes
- Commercial Boilers Firing Fuels Contaminated with Chlorinated Organic Wastes
- Forest Fires
- Apartment House Flue-fed Incinerators
- Agricultural Burning
- Landfill Flares
- Residential Oil Burners Burning Waste Oil

Rank D Source Categories
- Municipal Solid Waste (MSW) Incinerators
- Industrial Boilers Cofiring Wastes

* PCP = polychlorinated phenols

---

[1] This list of source categories undergoes constant review and revision and is subject to change.

Rank A - Large source categories (greater than 1 million tons of fuel and/or waste burned annually) with elevated dioxin precursor contamination or feed/fuel. These categories have a high potential to emit TCDD, and population exposure is expected to be relatively high compared to other source categories.

Rank B - Small source categories (less than 1 million tons of fuel and/or waste burned annually) or source categories with limited dioxin precursor contamination of feed/fuel. These categories have a high potential to emit TCDD, but population exposures are expected to be low.

Rank C - Source categories less likely to emit 2,3,7,8-TCDD.

Rank D - Source categories which have been tested three or more times.

2. It is assumed that the testing crew already has a working knowledge of all of the methods presented within. The document does present sufficient information to allow the user to select an appropriate sampling method during the development of the site-specific source test plan. The document allows the reviewers to follow the rationale used for selection of the location and sampling method.

Several other documents are being developed in conjunction with this sampling procedures document. These include a QA/QC Project Plan for the sampling effort, the Ash Sampling Program document, and site-specific test plans. Elements of each of these are addressed briefly in the following chapters.

1.1 APPROACH

This manual presents guidelines in several areas which are broken down into separate sections. First, the pretest site survey is discussed. The survey is where site-specific data is gathered prior to conducting the test. Next, specific sampling methods and some analysis methods are presented in Sections 3 through 5. These are broken down based on the physical form of the stream - gases, liquids and slurries, solids, sludges, and soils.

Design and operating data will also be necessary, and these requirements are presented in Section 6. A general approach to safety is contained in Section 7. Section 8 discusses QA/QC. Since a separate QA/QC plan will be prepared as part of the overall test program, this section presents the components of the plan but not a detailed compilation of the various techniques and forms that will be used. Similarly, a test plan will also be prepared for each specific source test, and Section 9 presents the specific features that will make up the test plan.

This document attempts to be as specific as possible when discussing techniques and making recommendations. However, so many decisions depend on the specific layout and operations of the facility that it is impossible to be completely specific. Obviously, there is judgment necessary that requires firsthand knowledge of the site. These kinds of decisions will be made in the test plan which is site specific. The purpose of this document is to provide guidance in making these judgment.

1.2 SPECIAL TERMINOLOGY

In the course of developing this manual of procedures for dioxin testing under Tier 4 of the National Dioxin Study, several terms unique to the study have been used. These terms are important to the understanding of the Tier 4 effort and the discussion of testing procedures applicable to combustion sources presented in the remainder of this document. Some of these important terms are defined below.

Troika - During the course of the National Dioxin Study, a number of dioxin analyses will be needed on a variety of samples. The EPA's Office of Research and Development (ORD) has been given the responsibility for all sampling and analytical guidance during the study. Furthermore, ORD will do the majority of the analytical work on the samples. To accomplish this task, three EPA laboratories have been chosen to conduct dioxin analyses. These laboratories are ERL-Duluth, ECL-Bay St. Louis, and EMSL-Research Triangle Park. Troika is the name chosen to refer to these three laboratories as a collective unit.

Sample Control Center (SCC) - All the tiers of the National Dioxin Study will be assisted in their scheduling and analysis activities by the Sample Control Center (SCC). Versar, Inc., 6850 Versar Center, Springfield, Virginia 22151, is the coordinator of the SCC. The SCC will provide episode numbers, track samples through the Troika, and provide assistance in shipping samples to the Troika.

2.0 PRETEST SITE SURVEYS

2.1 GENERAL

Prior to testing any facility, it is necessary to determine if testing is feasible and justified. This will occur during the pretest activities described in this section. The initial site screening phase will eliminate the obviously unsuitable sites from the overall list. Then a pretest survey of the remaining sites will be conducted to determine firsthand if the site can be adequately tested and to gather all information necessary to prepare a site-specific test plan.

The Tier 4 Project Plan identified eight general sample types that should be taken to characterize a given combustion source. These are listed in Table 2-1. One aspect of the pretest survey is to identify the specific sampling locations to be used during the test to acquire the sample types listed in Table 2-1, and to provide input for the selection of the appropriate sampling method. A second aspect is to develop information for the Sampling Control Center (SCC). The number and type of samples to be taken at a site must be provided to the SCC prior to initiating a test. Also, the Sample Control Center will assign an identification number based on the number and type of samples and inform Troika of any dioxin homolog analysis that will be needed. The QA/QC contractor also needs to know the number and type of samples to be taken in order to prepare and provide the correct number and type of control samples prior to the test.

The following sections describe how candidate sites will be identified and also discusses details of the pretest site survey.

2.2 INITIAL SITE SELECTION AND SCREENING

An initial list of sites will be compiled based upon in-house data compiled by Radian and inputs from the States and Regional EPA offices.

Sources for the data compiled by Radian will include background information and source category survey documents for several source categories and lists of contacts in various industries and trade groups. The background information documents combine data on source characteristics,

TABLE 2-1. RECOMMENDED SAMPLE SOURCES FOR CHARACTERIZATION OF TYPICAL COMBUSTION SOURCES

Source of Sample
Precombustion Air
Feed/Fuel
Stacks (before control)
Stacks (after control)
Bottom Ash
Ash from Pollution Control Device
Quench Water Effluent
Soils (in vicinity)

types of pollution control devices, source size, and location. Industry and trade group contacts can be used to identify facilities which may be interested in participating in the sampling program.

During the preparation of the initial list, the following factors will be considered:

1. The type of combustion device;
2. The waste materials or other fuels burned;
3. The size and age of the device; and
4. The current name, address, and telephone number.

After the initial list has been prepared, the candidate sites will be screened. The screening will focus on looking for combustion sources with the following broad characteristics.

1. The site or combustion source should be representative of the source category. For example, the combustion device should be combusting the same kind of waste fuel as the majority of the source category and should not be an outlier in terms of population and operating characteristics (age, size, design type, operating mode, etc.). Information concerning specific source characteristics will be compared to broad population characteristics which will be developed as part of the site selection process.

2. The combustion source should be testable without a lot of special equipment or modifications to the source. This includes appropriate sampling locations for all streams.

3. The combustion source (and control device) should be well instrumented. Key instrumentation would include methods to monitor and record fuel flow (waste and auxiliary fuel), combustion air flow or firebox oxygen content, firebox or bridgewall temperature, and steam or heat output. The pollution control device, if present, should be instrumented with respect to parameters which affect its operation, for example, scrubber pressure drop, liquor flow rate, etc.

4. The owners or operators of the facility should be willing to allow a test to be performed. This facilitates scheduling and data acquisition.

5. The presence of a pollution control device.

After screening the remaining candidate sites of interest will be contacted by phone to determine if they tentatively meet the characteristics listed above. In addition, the various regional and State offices where the sites are located will be contacted in order to gather as much additional information on each site as possible prior to the visit. It is anticipated that numerous sites will be dropped from further consideration based upon this preliminary screening. The preliminary list of candidate test sites will be constantly updated as the pretest planning and data gathering takes place. Additional candidate sites will be added as the need arises.

Initial efforts will concentrate on identifying candidate Group A sites (black liquor boilers, sewage sludge incinerators) and gathering data for them. The State and regional EPA offices' inputs will be important to provide a preliminary list of potential candidates to be screened.

Once a site or group of sites have been identified as being potential test sites and have passed all of the preliminary checks for representativeness, etc., the pretest survey will be scheduled. It is anticipated that three to four pretest surveys will be scheduled within a given week. This requires close cooperation between the facilities to be surveyed, Radian, and the Regional EPA office during the development of the survey schedule. In addition, site location and accessibility are important.

At the time of scheduling, a letter will be written to the facility operator. This letter will discuss the background and objective of the program, survey dates and will contain a list of typical information needs that will be sought at the survey.

Before traveling to a facility to be surveyed, survey personnel will review all readily available information on the facility and become familiar with the combustion device that is to be sampled and the nature of the waste or fuel being burned. This involves understanding the design and operating characteristics of the combustion device and the chemistry and operating characteristics of the process generating the waste streams being burned. An understanding of all phases of the facility operation will permit the team leader to make an initial selection of specific sampling locations.

Familiarization with the process is also necessary so that a checklist of the requisite data can be developed, including temperatures, pressures, flow rates, and variations of stream conditions with time, for the pretest survey.

2.3 FINAL SITE SELECTION

2.3.1 General

After establishing the necessary process data needs and selecting a tentative set of sampling points, a pretest site survey should be performed.

The pretest site survey team will typically consist of two people, usually an engineer and field testing specialist that are familiar with all the testing procedures and data needs and program objectives. At the test site, the team will meet with the plant engineer to verify the accuracy of the existing information and arrange for the acquisition of any missing data. A large facility may have several combustion devices operating simultaneously. The operating and design characteristics of each unit will be discussed with the plant engineer and the appropriate unit selected. In order to ensure that all of the data needed for evaluation of each candidate site is obtained during the pretest survey, a pretest survey form has been developed. A blank copy of this form is contained in Table 2-2. Prior to the survey, the form will be partially filled out with the site specific information available. All of this information will be reviewed with the facility engineer during the survey, and any data gaps will be filled.

Using the information obtained from the plant engineer along with detailed process flow diagrams, the survey team will then proceed to select the actual sampling sites with the following criteria in mind:

1. The sampling points must provide representative samples that can be handled by the standard sample acquisition and analysis hardware.

2. When possible, each sampling point should provide a representative sample of the streams. In some instances, streams from several combustion sources at a facility may be combined. Only one of the combustion sources may be the focus of the sampling program and, in this case, sample ports

TABLE 2-2. PRETEST SITE SURVEY FORM

GENERAL

Plant____
Address____
____
Phone______________________________Date of Survey____________
Latitude/Longitude or UTM_____________________________
Plant Personnel_______________________________________
Radian Personnel______________________________________
Other Personnel_______________________________________
Primary Plant Contact_________________________________
Phone (if different)__________________________________

SITE DESCRIPTION

Type of process_______________________________________
____
____
Operating Schedule____________________________________
____
____
Best Time to Test_____________________________________
Working Hours____
Shift Changes____

FACILITY DESCRIPTION

Combustion Device_____________________________________
____
Manufacturer____
Start-up Date____
Operating Schedule____________________________________
Capacity (lb steam/hr, Btu/hr, etc.)__________________
Fuel
  What Fuels are Burned_______________________________
  Fuel Source(s)______________________________________
  Does Fuel Vary (how, how much, how often)____________
  ____
  ____
  Potential for Fuel Contamination with Precursors____
  ____
  ____
Other Material Burned_________________________________
____
____
____
Typical Operating Conditions (flows, temperatures,etc.)__________
____
____
____
Duty Cycle
  Are there variable operating conditions or feed materials____
  If yes, what are they_______________________________
  ____
  Is the feed containing the precursors continuous or
  or intermitant______________________________________
Pollution Control Equipment Present___________________
____

TABLE 2-2. PRETEST SITE SURVEY FORM (CONTINUED)

____
____
____

Description of Ash Handling System____________________
____
____
____

Special Considerations, Operating History, Problems, Etc.________
____
____
____

AVAILABLE PROCESS DATA

Access to Design Data____________________
Access to O&M Logs____________________
Can we get blank copies of operator logs____________
Data Available From the Plant Instrumentation

Combustion Device____________________
____
____
____
____
____
____

Pollution Control Device____________________
____
____
____
____
____

How often is data entered into the operating log____________

DRAWINGS

A separate page will be provided for each of the drawings listed below.

Elevation drawing of the facility with dimensions shown
Plot plan of the facility with dimensions shown
Plot plans for soil and pond sampling
Map (plot plan) showing surrounding industry
Dimensioned sketches of sampling locations and hardware (as requ

FLOW DIAGRAMS

Flow diagram of combustion device and PCD showing sample locatio
This should include, at a minimum, sample locations for fuel, waste feeds, ash, flue gas, quench water and scrubber blowdown.

LIST OF SAMPLING LOCATIONS

MM5 Inlet____________________
MM5 Outlet____________________
CEM____________________
Process Streams____________________
____
____

____

____

MM5 SAMPLE POINT LOCATIONS AND DESCRIPTIONS

Sample point description____________________
Location____________________
Stack diameter (ft)____________________
Gas temperature ____________________
Gas static pressure____________________
Availability of sampling ports____________________
Diameter of sampling ports____________________
Nearest upstream disturbance (ft)____________________
Nearest downstream disturbance (ft)____________________
Power availability____________________
Scaffolding availability____________________
Lighting availability____________________
Compressed air availability____________________
Special space considerations____________________

Sample point description____________________
Location____________________
Stack diameter (ft)____________________
Gas temperature ____________________
Gas static pressure____________________
Availability of sampling ports____________________
Diameter of sampling ports____________________
Nearest upstream disturbance (ft)____________________
Nearest downstream disturbance (ft)____________________
Power availability____________________
Scaffolding availability____________________
Lighting availability____________________
Compressed air availability____________________
Special space considerations____________________

PROCESS SAMPLE POINT LOCATIONS AND DESCRIPTIONS

Sample Point Description (what is sampled, etc.)____________________
____
____
Location____________________
Process Stream____________________
Type of Material (gas, liquid, slurry, sludge, solid)____________________
Approximate % Water____________________
Physically, what is the sampling hardware(port, valve, nothing) and what is the size of the hardware____________________
____
____
____
Approximate Temperature and Pressure____________________

TABLE 2-2. PRETEST SITE SURVEY FORM (CONTINUED)

Sample Point Description (what is sampled, etc.)________________
____
____
Location____
Process Stream____
Type of Material (gas, liquid, slurry, sludge, solid)__________
Approximate % Water____
Physically, what is the sampling hardware(port, valve, nothing) and what is the size of the hardware_________________________
____
____
____
Approximate Temperature and Pressure________________________
____

Sample Point Description (what is sampled, etc.)________________
____
____
Location____
Process Stream____
Type of Material (gas, liquid, slurry, sludge, solid)__________
Approximate % Water____
Physically, what is the sampling hardware(port, valve, nothing) and what is the size of the hardware_________________________
____
____
____
Approximate Temperature and Pressure________________________
____

Sample Point Description (what is sampled, etc.)________________
____
____
Location____
Process Stream____
Type of Material (gas, liquid, slurry, sludge, solid)__________
Approximate % Water____
Physically, what is the sampling hardware(port, valve, nothing) and what is the size of the hardware_________________________
____
____
____
Approximate Temperature and Pressure________________________
____

Sample Point Description (what is sampled, etc.)________________
____
____
Location____
Process Stream____
Type of Material (gas, liquid, slurry, sludge, solid)__________
Approximate % Water____
Physically, what is the sampling hardware(port, valve, nothing) and what is the size of the hardware_________________________
____
____

TABLE 2-2. PRETEST SITE SURVEY FORM (CONTINUED)

Approximate Temperature and Pressure____

CONTINUOUS MONITORING CONSIDERATIONS

Location(s)____
Gas Temperature____
Gas Pressure____
Length of sample line necessary____
Expected concentration ranges:
CO:____
CO2:____
SO2:____
NOx:____
O2:____
THC:____

MOBILE LAB AND OTHER SUPPORT FACILITIES

Space Available (where, how much, show on plot plan drawing)____
Available Utilities
Electrical (voltage, amperage, phase for each circuit)____
Other____
Generator operation OK?____
Area for temporary equipment and sample storage____
Other Support Facilities
Phone available____ Number____
Access to Copier____
Access to Office Space____

SPECIAL REQIREMENTS AND SITUATIONS

Scaffolding Requirements____
Other Special Access Requirements____
Special Safety Requirements____
What is required to obtain access to plant (letters, agreements,
Confidentially Issues____
Other____

downstream of where the streams combine will be of no value. Provisions for installing additional sampling points will be discussed with plant personnel at this time.

3. The sampling site must have a reasonably favorable working environment. The survey personnel must consider what the temperature and noise levels are in the sampling areas; if protection from rain, snow or strong winds exists; and whether scaffolding, ladders, pulleys, etc., exist and are safe.

The identification of support facilities and services is an essential aspect of the site survey. In an effort to minimize the requests made upon the operators and to minimize scheduling problems for these support services, it is desirable that the on-site laboratory operate completely independently of external support facilities. The pretest site survey form will specifically request this information; e.g., the availability of electrical service.

The results of the pretest site survey must be sufficiently detailed so that the correct process stream, the proper sampling location and, the appropriate methodology will be completely defined prior to arrival of the field test team at the source site. For this reason, the following sections detail information that will be obtained during the survey for each sampling location.

2.3.2 Sampling for Gaseous and Particulate Emissions from the Combustion Device and Control Device

During the pretest survey, the surveyor will perform the following steps:

1. Trace the flow of combustion gases from the combustion device through the heat recovery devices and control devices. This involves a physical inspection of the ductwork from the combustion device to the stack.

2. Locate and itemize control devices, stacks, and sampling locations.

3. Record the physical parameters of the gas streams in as much detail as possible. For example, these can include temperature pressure, physical nature, flowrate, flow disturbances, etc.

4. Prepare sketches of the overall area. Include elevation and plot plan with dimensions.

In performing the pretest site survey, the crew will verify the existence of the following requirements for stack gas sampling:

1. The sampling ports: To accommodate the sampling probe, the port must have an opening of at least 2-1/2 inches. A 3-inch nipple welded to the stack is usually the best way to obtain access.

2. The test platform: The size of the test platform, which supports the sampling equipment and test personnel, depends on the length of the probe to be used. However, a platform of normally 5 ft x 4 ft is usually adequate. Also, there should be a clearance of 1.5 to 2.0 stack diameters out from the sampling point to accommodate the sampling probe.

3. Electrical power: Power is required for the probe and oven heaters and for the vacuum pumps. To operate the entire system, a total of two 20-amp circuits adjacent to the sampling locations and one 20-amp circuit by the mobile lab parking area are required.

2.3.3 Liquid and Slurry Sampling

The liquids and slurries that may have to be sampled include auxiliary fuels, waste materials that are combusted, make-up water, scrubber water, ash sluice water, and ash slurries. The number and type of liquid or slurry streams that have to be sampled will differ from site to site.

The same general criteria for locating a gas sampling point can be applied to locating sampling sites for liquid samples. A review of those criteria and procedures is contained in Section 2.3.2 of this chapter.

While the site selection criteria for gas and liquid sampling are generally the same, the test personnel must be aware of the problems associated with the sampling of liquids and how these factors affect the choice of a sampling site. Two factors will affect the selection of a sampling site for liquid/slurry streams:

1. Stream homogeneity: This is the most important problem that must be addressed by the site survey crew. Unlike gas streams, which mix fairly evenly, liquid streams tend to be more stratified because of lower thermal agitation and higher fluid viscosities.

2. Stream flow rate: Large, slow-moving streams will offer more of a chance for stratification to occur. This factor is especially important in large pipes or open sluices and ditches.

Based on the stream properties, primarily whether it is a homogeneous liquid or a slurry, the site survey should determine if the sampling provisions are sufficient. For example, for a slurry stream it should be located in a well-mixed zone such as after a pump. This decision will vary from site to site and should be made on the basis of good technical judgment.

2.3.4 Solid Sampling

Solid input and output streams in most combustion devices consist of wastes used as fuels, bottom ash, and collected particulates. These solids range from very fine powders to very coarse lumps depending upon the combustion device and the control device. This variation in sample consistency influences the sampling technique to be used, which must be established in the pretest site survey. For purposes of the pretest site survey, therefore, the following questions must be answered:

1. Can the material be sampled as it enters or leaves the process, or must it be sampled in its stored or piled form?

2. If material can be sampled as it enters or leaves the process, what is the nature of the conveyor system (belt, worm screw, pan), and what is the closest available sampling location to process entry?

3. What is the consistency of the material (powder, coarse grain, lump), and what is the apparent (visual) variance within this consistency?

4. What is the approximate size of the storage reserve, and what is the method of access to said reserve?

2.3.5 Soil Sampling

Soil sampling will be conducted at all sites selected for full scale testing. As part of the pretest survey, a plot plan of the facility will be obtained. This plot plan will be used to develop the soil sampling grid. During the pretest survey, observations will be made of the soils adjacent to the fuel/waste storage and ash disposal areas. Any contamination or spillage should be noted.

2.3.6 Pretest Survey Forms and Reporting

After the pretest site survey, a brief trip report will be prepared that describes the design and operation of the combustion source. The purpose of the report is to document the pretest survey and to provide recommendations concerning the suitability of the site for testing. The completed pretest survey forms will provide the basis of the report. Despite individual variations, all trip reports must address key information areas. The headings listing below should be used as a checklist to ensure that all relevant items are reported:

1. Site visited - name, location, type (e.g., black liquor boiler, wire reclamation incinerator);
2. Inclusive dates of visit;
3. Persons conducting survey, persons interviewed, or otherwise supplying data or information (name, title, telephone number);
4. Facilities, processes, and equipment observed;
5. Information acquired on the combustion process:
   - Source of fuel and waste materials combusted;
   - Design data, age, size, manufacturer, type of device;
   - Operating conditions;
   - Operating history;
   - Process parameters;
   - Characteristics of streams to be sampled (physical form, temperature, pressure);
   - Operating schedule including schedule outages and abnormal operations;
   - Emission rates, controlled and uncontrolled; and
   - Pollution control system(s) - operating parameters, efficiencies achieved, and data from relevant past tests.
6. Recommendations concerning testing.

At the conclusion of the pretest survey, the facility will be asked to identify any inaccuracies or confidential data included in the pretest survey form. If none of the information supplied by the facility is confidential, it will be indicated as such in the trip report.

Following the pretest survey, each site will be evaluated for its appropriateness for inclusion as a test site. It is possible that sites will be selected prior to completion of all pretest surveys. Selection of sites will be made in conjunction with the EPA Project Officer.

Following selection, candidate sites will then be notified and test dates will be scheduled. A site specific source test plan will be prepared for each site. This will include a table detailing the number and type of samples to be taken. The Sample Control Center will be sent a copy of the sample matrix and will be asked to supply an episode number. Sample identification numbers will then be assigned by Tier 4 EPA personnel.

3.0 GASEOUS STREAMS - SAMPLING AND ANALYSIS

This section describes the sampling techniques that will be used to measure specific gaseous and particulate emissions from combustion sources as part of the Tier 4 sampling program. Section 3.1 discusses the types of streams that are anticipated. Section 3.2 presents the recommended sampling techniques and instrumentation. The techniques are described in more detail in Section 3.3.

3.1 GASEOUS EMISSIONS SOURCES

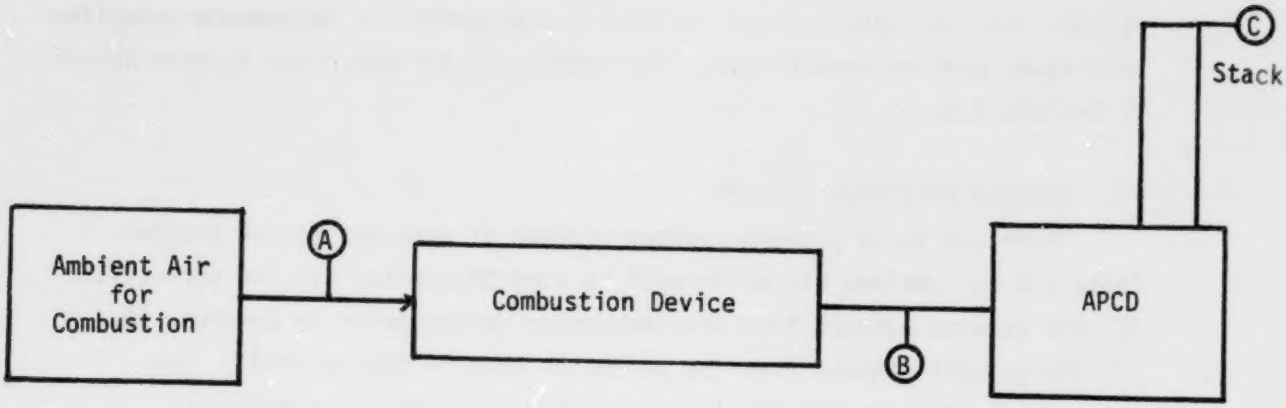
There are three primary gaseous streams of interest to the program. These are (a) ambient air which will be used to provide air for combustion, (b) the gaseous exhaust from the combustion device prior to control, and (c) the gaseous exhaust from the pollution control device (PCD). The gaseous streams from a typical combustion device are illustrated in Figure 3-1. The parameters to be measured for each of these three streams are listed in Table 3-1.

In addition to taking grab samples of gases for PCDD and other analyses, continuous monitoring of the combustion gases will be performed. Depending on the specific type of combustion source and fuels utilized, the parameters monitored may vary slightly.

3.2 RECOMMENDED SAMPLING TECHNIQUES

A variety of gaseous sampling techniques will be necessary including manual sampling from stacks, continuous monitoring (CEM) from stacks and high volume sampling of the ambient (combustion) air. The variables to be measured with the recommended sampling and analysis techniques are presented in Table 3-1. Outlet streams will be sampled for the presence of dioxins. In addition, O_2 will be measured at the outlet of the combustion device. The combustion air will be sample for dioxins and precursors if they are suspected to be present.

As shown in the table the stack will be analyzed for several additional compounds. Some of these shown are only applicable for some sources since they provide information on the process performance but do not directly


C
Stack
A
Ambient Air for Combustion
Combustion Device
APCD
B

Sample Points

A - Ambient air
B - Uncontrolled gaseous emissions
C - Controlled gaseous emissions

Figure 3-1. Gaseous streams associated with combustion sources.

TABLE 3-1. PARAMETERS TO MEASURE IN GASEOUS STREAMS

Stream	Parameter	Sample Collection Method
Precombustion Air	Dioxin[1,2]	Ambient XAD Train[3]
	Precursors[2]	Ambient XAD Train[3]
Combustion Device Outlet	Dioxin[1]	MM5T[4]
	Moisture	EPA Method 4
	Particulate[2]	EPA Method 5
	Molecular weight	EPA Method 3
	Volumetric flow	EPA Method 2
	HCl	Acid Train
	CO	Continuous Monitor
	CO_2	Continuous Monitor
	O_2[2]	Continuous Monitor
	Sulfur oxides[2]	Continuous Monitor
	Nitrogen oxides[2]	Continuous Monitor
	Total Hydrocarbon	Continuous Monitor
Stack Exhaust[5]	Dioxin[1]	MM5T
	Particulate[2]	EPA Method 5
	Volumetric Flow	EPA Method 2
	Molecular Weight	EPA Method 3
	Moisture	EPA Method 4
	HCl[2]	Acid Train

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[1] Dioxin - 2,3,7,8 TCDD plus homologues (polychlorinated dibenzo-p-dioxins with three to eight chlorines).

[2] Where applicable, see text.

[3] Ambient XAD train - an ambient air sample train used in conjunction with an XAD-2 trap.

[4] MM5T - a modified EPA "Method 5" train as defined in the ASME protocol.

[5] In some cases, similar measurements may not be made at both the combustion device outlet and the stacks exhaust. In these cases some of the stack exhaust measurements will not be made.

assess dioxin emissions, but are commonly gathered during CEM programs. HCl, SO_x and NO_x are often measured, but have no direct relationship with dioxin emissions and are fuel dependent.

Table 3-1 shows that measurement of SO_x, NO_x, and particulate will be made where useful. These components are often measured, but do not always provide useful information for all combustion sources. NO_x can be an indicator of combustion conditions; however, if the fuel nitrogen varies substantially it is difficult or impossible to compare firing conditions on the basis of NO_x. A rough indicator of particulate concentration is obtained with MM5; however, if very accurate measurements are desired, the regular EPA Method 5 should be used. HCl is shown as required since chlorine concentrations may give some clues toward evaluating dioxin formation. However, there may be situations, such as downstream from a scrubber, that this measurement may not be useful and, in these cases, the HCl measurement can also be considered optional. Therefore, it is recommended that the measurement of these compounds be decided for each source test based on the value of the data collected.

For continuous monitoring the recommended sampling technique is to extract gas with a heated sample line and condition it prior to introducing it to the instruments. This is described in more detail in Section 3.3. The recommended analytical techniques for the CEM system are shown in Table 3-2. In general, there are three areas of gaseous sampling techniques that will be utilized in the program. These are manual techniques, continuous monitoring techniques, and ambient techniques. The general application of each of these techniques will be discussed in this section.

3.2.1 Ambient Techniques

There is only one ambient sampling technique that will be used in the sampling program. This technique will be used to sample combustion air at sites where the ambient air potentially contains detectable levels of dioxin or its precursors. The sample will be collected on an XAD sorbent trap using a sampling train similar to Modified Method 5.

TABLE 3-2. RECOMMENDED CONTINUOUS MONITORS FOR TESTING TIER 4 COMBUSTION SOURCES

Pollutant Species	Model	Operating Principle
O_2	Beckman No. 755 or 752 (or equivalent)	Paramagnetic
NO_x	Teco Model No. 10 (or equivalent)	Chemiluminescence
THC	Beckman Model No. 406 (or equivalent)	Flame ionization
SO_2	Teco Model No. 40 (or equivalent)	Pulsed fluorescence[1]
CO/CO_2	Anard Model No. 702 (or equivalent)	Nondispersive Infrared
Molecular weight	Shimadzi 3BT (or equivalent)	Gas Chromotography - Thermoconductivity Dectector

[1] Note - Pulsed fluorescence measurements are affected by O_2 and CO_2 in the flue gas. Therefore, these instruments should be calibrated with gases that contain O_2 and CO_2 concentrations similar to the source. Alternatively, an instrument specific equation can be used, if available.

A schematic diagram of the "ambient XAD" sample train is shown in Figure 3-2. The train consists of a probe, condenser/sorbent tube, water knockout trap, silica gel container, transfer line, pump, and dry gas meter. Ambient air will be drawn into the sorbent module, where it will be cooled to 68°F or lower, and the organic constituents will be adsorbed by the XAD resin. The gas will then be dried with the silica gel and the sample volume measured by the dry gas meter. Two separate sample trains will be run simultaneously. One of the XAD tubes will be analyzed by Troika for total TCDD, and the other tube will be analyzed for dioxin precursors at Radian's RTP laboratory.

The entire ambient XAD sample train will be leak tested before and after each test run at 10 inches H_2O to ensure that the total leakage is less than 0.02 cfm. The ambient XAD sample train will be operated during the same time periods that the MM5 samples are being collected. However, the same set of ambient XAD traps will be used for all three MM5 test runs, thus providing a composite combustion air sample for each site. The reason for doing this is that ambient concentrations are very low, and this approach will allow very low concentrations to be measured. In addition, it reduces the overall analytical load by requiring only a single extraction and analysis. The dry gas meter reading will be recorded twice daily at the beginning and end of each test period. The dry gas meter temperature, pressure, and volume will be recorded at least once per hour during the sampling periods. Since the XAD trap has a limited capacity, it will be necessary to calculate a maximum throughput based on conservative assumptions of the ambient TCDD and dioxin precursors. Each of the three test runs will involve pulling one-third of this calculated volume through the XAD trap.

3.2.2 Manual Techniques

There are several manual testing techniques that will be used in the Tier 4 sampling program. Each technique is designed to measure a specific parameter. The stack techniques to be used in the Tier 4 sampling program are ASTM-MM5T, EPA Reference Methods 1-5 and a HCl Acid Sampling train. The

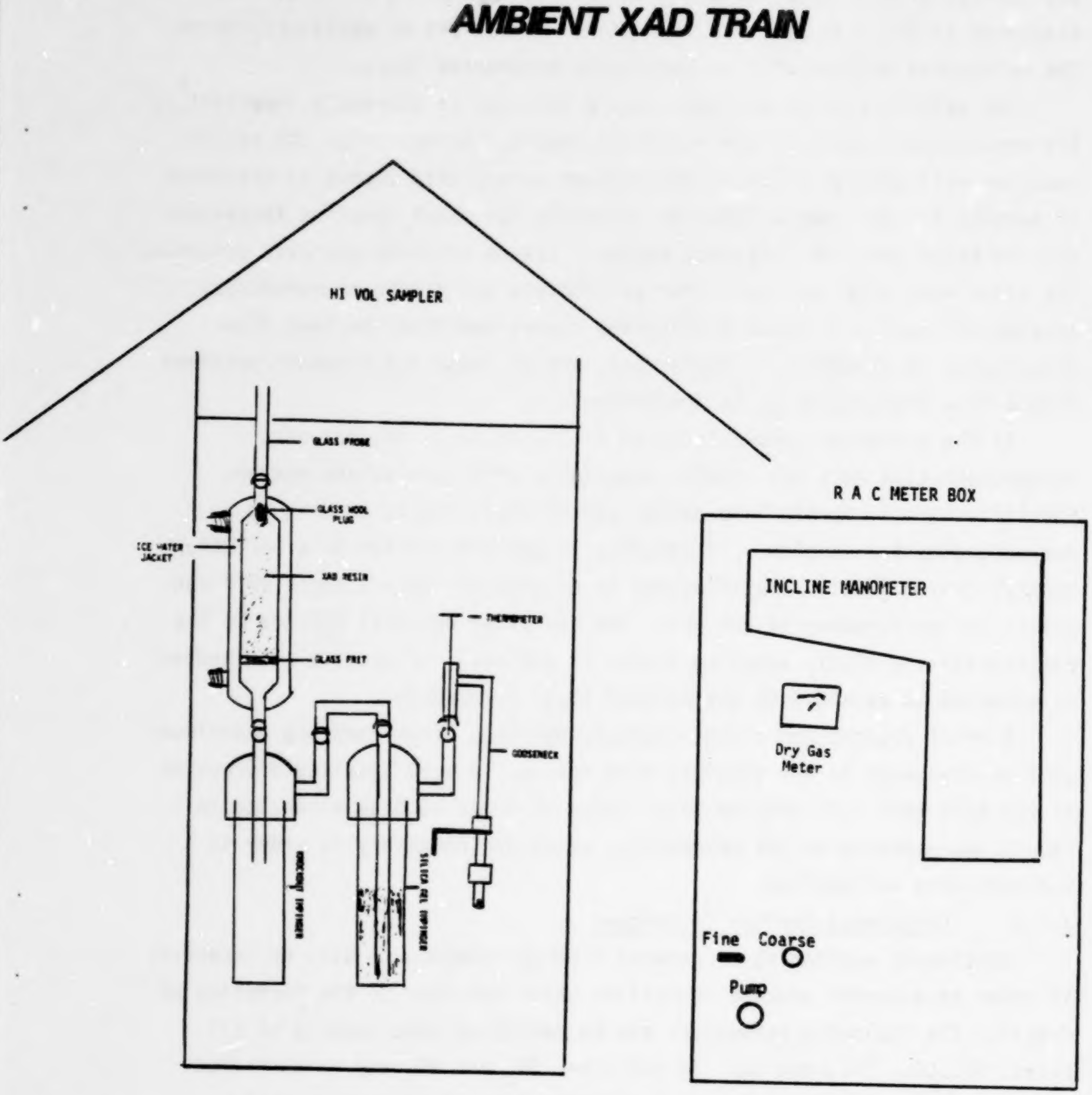

AMBIENT XAD TRAIN
HI VOL SAMPLER
GLASS PROBE
GLASS WOOL PLUG
ICE WATER JACKET
XAD RESIN
GLASS FRIT
THERMOMETER
GOOSENECK
KNOCKOUT IMPINGER
SILICA GEL IMPINGER
R A C METER BOX
INCLINE MANOMETER
Dry Gas Meter
Fine
Coarse
Pump

Figure 3-2. Schematic diagram of the ambient XAD sample train.

application of each specific train to the stack sampling ports will be discussed in the site specific test plan. Variations of modifications to the referenced methods will be thoroughly documented there.

The selection of an adequate sample location is extremely important in the representativeness of the resultant sample. Selection of the sample location will be made based on the pretest survey trip report as discussed in Section 2. All sample location selection for stack sampling techniques will be based upon EPA Reference Method 1 citing criteria whenever possible. The stack must have two ports (for particulate and dioxin measurements) located 90° apart, at least 2 diameters downstream from the last flow disturbance (8 diameters is preferred), and at least 1/2 diameter upstream from a flow disturbance (2 is preferable).

If the preferred sample location siting criteria are not met, unrepresentative data may result, especially with particulate matter. Stratification of particulate matter can be significant, leading to nonrepresentative samples. If sampling is performed prior to a pollution control device (PCD), stratification is of greater concern since this can affect the performance of the PCD. The use of an optional cyclone in the particulate and dioxin sampling trains is advisable if particulate loading is expected to exceed 0.05 grains/dscf (0.11 grams/dscm).

A brief description of the commonly utilized stack sampling techniques will be discussed in the sections with follow. A more detailed discussion of the ASME-MM5T will also be highlighted in order to draw attention to recent improvements to the methodology which are necessary in order to minimize data variability.

3.2.3 Continuous Monitor Techniques

Continuous monitoring of several flue gas components will be necessary in order to document process conditions which may lead to the formation of dioxin. The following parameters may be monitored continuously at all sites: CO, CO_2, THC, and O_2. In addition, SO_x and NO_x may be monitored continuously where appropriate. A specific list of parameters will be finalized in each site specific test plan. The ASME conference on development of dioxin test methods for energy from solid waste combustion plants suggested that, in addition to the parameters listed above, water and opacity be continuously monitored. However, these parameters will not provide useful information for most Tier 4 sources. They will be difficult to measure at sites where limited suitable sample locations are availabe for temporary monitors. This is often the case. For sources equipped with permanent, in-stack monitors for opacity and H_2O, copies of the chart records will be obtained for the test period. Where these are not available, the gas phase H_2O concentration will be determined from the MM5 results. The types of recommended continuous monitors that are recommended are shown in Table 3-2.

The operation of the continuous monitors is further discussed in Section 3.3. The detailed specifics of operation will be further defined in the site-specific test plan, once details of the sample stream are determined.

3.3 DESCRIPTION OF SAMPLING TECHNIQUES

3.3.1 Manual Sampling Methods

This section contains a brief narrative of each manual sampling method anticipated for Tier 4 gaseous sampling. Where applicable, special notes are included in italics to indicate a particular caution or advisable modification. If more detailed description of the individual methods are required, the citation listed in the Federal Register should be consulted.

EPA Reference Method 1

The criteria described in EPA Reference Method 1 (Sample and Velocity Traverses for Stationary Sources, Federal Register 42 FR 41754, August 18, 1977) will be used to select appropriate sampling sites whenever possible. The 8 diameters and 2 diameters rule, upstream and downstream respectively, of any flow disturbance is the primary criteria needed to be met. The minimum allowable is 2 diameters upstream and 0.5 diameters downstream.

EPA Reference Method 2

EPA Reference Method 2 (Determination of Stack Gas Velocity and Volumetric Flow Rate, Federal Register 42 FR 41759, August 18, 1977) will be followed to determine flue gas velocity, stack temperature, stack pressure, and volumetric flow rate. All flue gas volumetric flow rates will be reported for both actual and standard conditions. Standard conditions will be 68°F and 29.92 inches of mercury (Hg). Equipment utilized by this method (Type S - pitot tube, differential gauge, barometer and temperature gauge) will meet or exceed the specifications called for in the reference document. Appropriate calibration procedures will be executive on all equipment utilized prior to use in the field.

EPA Reference Method 3

EPA Reference Method 3 (Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight, Federal Register 42 FR 41768, August 18, 1977) will be utilized to characterize the stationary gas analysis. As permitted under Section 1.2, paragraph 2 of the referenced document, a modification to the sampling procedures and use of an alternative analytical procedures will be implemented. A single point integrated sample is anticipated. In lieu of an Orsat analyzer, a gas chromatograph with a thermal conductively detector (GC/TCD) will be utilized to measure the concentrations of oxygen (O_2), carbon dioxide (CO_2), nitrogen (N_2), and carbon monoxide (CO) in the integrated bag sample. Previous test programs have demonstrated the acceptability of this substitution. This alternative analytical method offers acceptable accuracy and a permanent hard copy record of the analysis. The data will be reported in units of percent by volume for O_2, N_2, and CO. Dry molecular weight will be calculated by Equation 3-2 of the referenced document and reported in units of grams per gram-mole (g/g-mole).

EPA Reference Method 4

EPA Reference Method 4 (Determination of Moisture Content in Stack Gas, Federal Register 42 FR 41771, August 18, 1977) will be utilized to measure volumetrically the moisture (H_2O) content of the flue gas streams. The sampling train specified in EPA Method 5 will be utilized to measure moisture in conjunction with particulate matter determinations. This is an acceptable procedure under Section 2, paragraph 1 of the referenced document. All components shall be maintained and calibrated according to the procedure outlined in Method 5. The moisture content (B_{ws}) will be reported in units of proportion of water vapor, by volume, in the gas stream according to Equation 4-4 of the referenced document.

HCl Acid Sampling Method (Gaseous)

The sampling procedure developed for the determination of hydrogen chloride emissions from stationary sources is basically a modification of the standard procedure for SO_2 determination (EPA Reference Method 6). The HCL method utilizes the same equipment (i.e., probe, glassware, pump, dry gas meter, etc.) with the exception that a regular midget impinger is used for the first impinger in place of the midget bubbler used in Method 6. (At the option of the tester, regular size Method 5 glassware may be utilized.)

Dilute sodium hydroxide (0.1m NaOH) is used as the absorbing solution in the impingers. (If higher levels of CO2 (<15 percent are expected for sample periods greater than 1 hour in duration, the tester may choose to replace the NaOH with sodium acetate, in order to prevent plugging of the impingers due to formation of carbonate precipitate.

A heated glass lined probe is used with the temperature maintained at 300°F or at stack temperature whichever is greater. A pyrex wool plug is inserted in the inlet end of the probe in the same manner as required by Method 6. It is important to note that if this method is used downstream of a wet scrubber that the probe and filter must be heated to avoid condensation. This temperature should be 25° to 50°C above the dewpoint. The impinger train is immersed in an ice bath during sampling. The impingers containing the absorbing solution are connected to the probe with glass connectors and U-tubes held in place with standard pinch clamps. The first two impingers contain the absorbing solution. The third impinger is empty, and the fourth impinger contains silica gel to remove moisture. A standard umbilical line is used to connect the impingers to a standard control module containing the pump and dry gas meter.

Samples collected in this manner will be analyzed remotely by ion chromatograph. The analysis results in conjunction with the dry gas meter reading can be used to determine the gas phase concentration.

ASME-MM5T

EPA Method 5 is the basis for the ASME train for sampling for dioxin. There are a variety of modifications to the standard Method 5 sampling train, each of which has a selected objective in mind. The ASME-MM5T that will be utilized for Tier 4 reflects the latest draft of the ASME dioxin sampling protocol which is attached as Appendix A.

The ASME-MM5T consists of the following components:

- probe,
- cyclone (optional),
- glass filter holder with Teflon seal,
- glass condenser coil,
- sorbent trap (XAD-2),
- water knock out trap (optional),
- two water filled impingers,
- empty impinger,
- silica gel impinger, and
- pump and dry gas meter.

The front half of the sampling train (probe and filter) should be maintained at 248°F to prevent moisture condensation and to allow for a determination of dioxin in the front half particulate matter if desired. All connections of glassware must be made grease-free. (If the glassware had been previously used with grease, a special cleaning procedure must be followed in order to prevent interferences in the analytical screening.)

Acceptable materials of construction for any part of the sampling train that contacts the sample may be either glass or TFE Teflon. (Stainless steel is not regarded as an acceptable material for either the probe or filter housing, if avoidable.)

The sampling train should be operated isokinetically at a sample location which meets EPA Method 1 siting criteria for particulate matter determinations. The sample location should be traversed following normal particulate sampling protocol as specified in EPA Method 5. The gas flow rate through the sample train should range between 0.014 to 0.028 cm/min (0.5-1.0 cfm), by selection of appropriate sized sampling nozzle. The ASME

Committee responsible for development of the dioxin sampling method (MM5T) has recommended a sampling time of eight hours which is equivalent to sample volume of approximately 13 dscm. The intent is to produce enough sample to allow detection of 1 ng of dioxin in the train. Extended periods of sampling will be required (~ 8 hours), exclusive of setup and sampling recovery.

Precautions in leak checking the train must be taken. If the leak free operation cannot be achieved on the first attempt, a filtering apparatus to clean the ambient air being drawn into the sample train during the leak check should be considered. The ambient organics concentration at some industrial locations may be greater than those found in efficiently operated combustion sources and, therefore, be a potential source of contamination.

Sealing greases should not be used on the sample train during operation or cleanup.

Hexane rinsed aluminum foil should be used to cap off all connections prior to and after sampling. Contact with unwashed surfaces must be avoided.

3.3.2 Continuous Gas Monitoring

Continuous monitoring sampling system for the following flue gas parameters will be conducted during each test period: CO, CO_2, O_2, NO_x, and total hydrocarbons (THC). These and other parameters were recommended by the ASME consensus committee, and will be used to indicate combustion conditions during the period of the test. For example combustion efficiency can be calculated using CO & CO_2, and stack oxygen levels can be used as an indication of the amount of O_2 available for combustion.

This section describes suggested continuous monitors for application to the National Dioxin Study at combustion sources within Tier 4. The previous section listed recommended monitors for all purposes of the study.

Additional continuous monitoring of the flue gas may be appropriate for specific sites where information exists which indicates additional parameters are warranted. An example is SO_x where high levels of sulfur are present in the feed or fuel. Additions or substitutions to this list of continuous monitors will be discussed and justified in the site-specific test plan for individual combustion sites.

Figure 3-3 is an example schematic of an acceptable continuous emission monitor system (CEMS) for installation during the test program. A separately installed continuous monitor system will be used during the test program. The site-specific test plan will include a schematic diagram similar to the one shown in Figure 3-2 which indicates the sampling location(s) and means of transport and introduction of sample to the analyzers. For gas conditioning, a TECO Model 600D is recommended.

There are several areas of concern which should be addressed in the site-specific test plan regarding the design of the continuous monitor system. These include the following:

- The heating capacity of the sample line (300°F recommended);
- Cleaning of the heat-traced sample line;
- The uptake of all the analyzers and the capacity of the sampling line and gas conditioner to supply sufficient volume to the same manifold. The recommended list of analyzers requires that heat-traced sample line be of at least 3/8-inch diameter;
- The expected concentration of each species at each sample location in order to specify suitable gas calibration standards and instrumental ranges.
- The certification/calibration procedures which will be used on-site to qualify the recorded data; and
- The data handling and recording system.

3.4 CLEANING PROCEDURES

The sampling containers and sampling equipment should be cleaned prior to the test by the procedures listed in Table 3-3. The cleaned containers will be transported to the sampling location with the Teflon^R lids tightly in place. Once the sample is introduced to the container, the lid shall be replaced and wrapped with clean Teflon^R tape, wrapped in cleaned foil, and transported to the analytical locations.

Sampling equipment for each test will be precleaned, capped with aluminum foil, and packaged for transportation to the field. New, precleaned train components including the filter holder and the XAD-2 trap

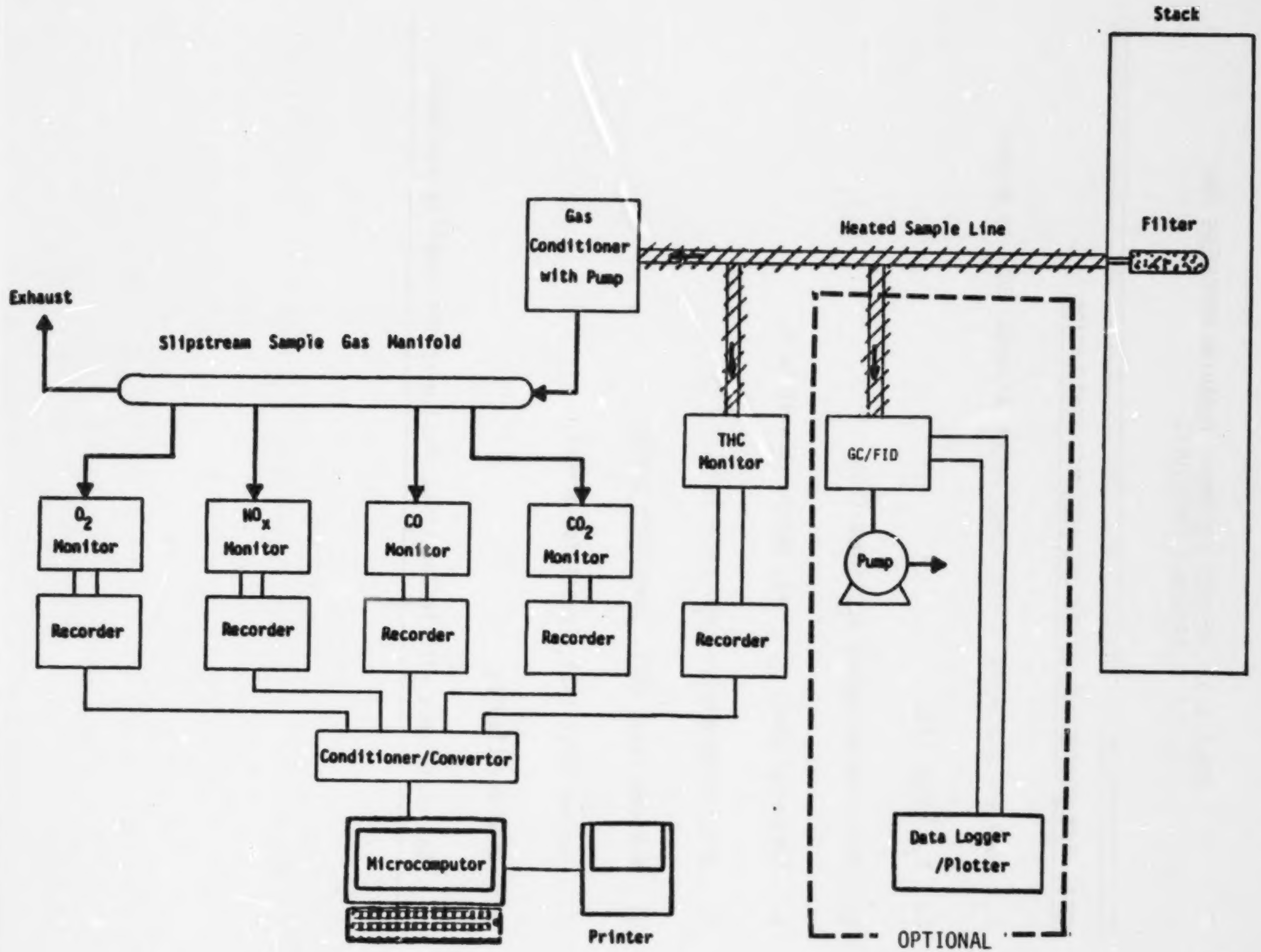

Stack
Filter
Heated Sample Line
Gas Conditioner with Pump
Exhaust
Slipstream Sample Gas Manifold
O_2 Monitor
NO_x Monitor
CO Monitor
CO_2 Monitor
THC Monitor
GC/FID
Pump
Recorder
Recorder
Recorder
Recorder
Recorder
Conditioner/Convertor
Microcomputor
Printer
Data Logger /Plotter
OPTIONAL

Figure 3-3. Gas conditioning.

TABLE 3-3. PRETEST EQUIPMENT CLEANING PROCEDURE FOR SAMPLING CONTAINERS

NOTE: USE DISPOSABLE GLOVES AND ADEQUATE VENTILATION

1. Soak all glassware in hot soapy water (Alconox) 50°C or higher.
2. H_2O rinse (X3).
3. Distilled/deionized H_2O rinse (X3).
4. Chromerge rinse if glass, otherwise skip to 6.
5. Distilled/deionized H_2O rinse (X3).
6. Acetone rinse (X3), (pesticide grade).
7. Hexane rinse (X3), (pesticide grade).
8. Oven dry (110°C).
9. Cap containers with Teflon lids. Foil wrap the sampling equipment.

will be used for each test. When going to a new location, the cleaning of nonreplaceable components such as the probe and condenser shall consist of:

1. Removal of loose sample,
2. H_2O Rinse (x3),
3. Acetone rinse (x3) (pesticide grade),
4. Hexane rinse (x3) (pesticide grade),
5. Air dry in a clean environment, and
6. Foil wrap (hexane rinsed).

Between sampling at the same location, no extra cleaning is necessary.

3.5 SAMPLE FREQUENCY

These are recommended frequencies for planning purposes. However, if more frequent samples can be obtained and are justified, it is reasonable to change the sample frequency.

3.6 REPORTING FORMAT

In order to aid consistency between the various tests, a standard format is recommended for reporting the results. For gaseous analyses, it is recommended that the report consist of a table as shown in Figures 3-4 and 3-5. Similar tables should be prepared for each sample point. Additional forms of reporting, such as hourly and daily averages or a summary of dioxin measurements at each location should also be considered. The results should also be reported on the basis of plant throughput, e.g., kg per ton of feed or kg per million Btu of heat input. The specific format and method of calculating this value will depend on the type of process being evaluated.

A more detailed description of the reporting guidelines can be found in the publication National Dioxin Study Tier 4 - Combustion Sources Dioxin Source Test Reporting Format Guide, EPA-450/4-84-014f, November 1984, Draft.

CRITERIA POLLUTANT ANALYSES

Sample Location:

Date-Date	Time	Moisture %	Part, gr/dscf (by Method 5)	Flue Gas Flow, dscf/min	CO, ppm	CO_2 ppm by vol	O_2 % by vol	SO_x ppm by vol	NO_x ppm by vol	HCl ppm by vol

Figure 3-4. Formats for reporting individual data from stack samples.

Location/ Compound	Test Date	Sample Volume (DSCM)	Compound* Quantity In Sample Volume (ng)	Stack Flow Rate (m^3/min)	Concentration in Stack Gases (ng/m^3)	Emission Rate (mg/hr)	Emission Rate of Waste Fuel Fired (µg/kg)
Location A - Test 1							
2,3,7,8-TCDD							
Tetra-CDD's							
Penta-CDD's							
Hexa-CDD's							
Hepta-CDD's							
Octa-CDD's							
Total CDD's							
Location A - Test 2							
2,3,7,8-TCDD							
Tetra-CDD's							
Penta-CDD's							
Hexa-CDD's							
Hepta-CDD's							
Octa-CDD's							
Total CDD's							
Location A - Test 3							
2,3,7,8-TCDD							
Tetra-CDD's							
Penta-CDD's							
Hexa-CDD's							
Hepta-CDD's							
Octa-CDD's							
Total CDD's							
Average of 3							
2,3,7,8-TCDD							
Tetra-CDD's							
Penta-CDD's							
Hexa-CDD's							
Hepta-CDD's							
Octa-CDD's							
Total CDD's							

---

*The quantity of each compound will be provided by the Troika Labs. All other data and calculations will be done by test contractor.

Figure 3-5. Data reporting format for dioxin analysis.

4.0 SAMPLING LIQUIDS AND SLURRIES

Liquids and slurries will account for a number of samples at many combustion devices/facilities. Liquids are defined as sample streams having a moisture percent greater than 90 percent. Slurries are defined as samples with moisture content greater than 70 percent but less than 90 percent and having visible suspended solids. Slurries can be thought of as an easily flowing material with entrained particulate matter.

Different sampling techniques are used for collecting liquids than for slurries. Since there may be some particulate matter in a liquid sample, it should be taken from a point in the stream where there is good mixing. Stratification of the stream is usually not a problem if the stream is moving. Slurries, on the other hand, can stratify on impact with the walls in the elbows or bends in piping. Care must be taken to obtain these samples at straight pipe runs where the mixing is good (Reynolds Number >2500).

In order to obtain a representative sample of liquids/slurries, three main objectives must be met:

- Choose a sample point which will allow the most representative sample to be obtained;
- Choose a sampling technique appropriate to the sample point; and
- Prepare composite samples based on the conditions of the stream and flow.

These main objectives will be discussed in the following subsections.

4.1 SOURCES OF TYPICAL LIQUID/SLURRY STREAMS

Figure 4-1 shows a schematic of a hypothetical plant to be sampled for this study. The figure shows more sample points than would be present on a real plant, but they are put in here to show the possible liquid/slurry streams and the sample locations. The actual streams to be sampled should be determined as part of the preliminary evaluation of the process streams during the pretest survey. Similarly, decisions as to whether the existing

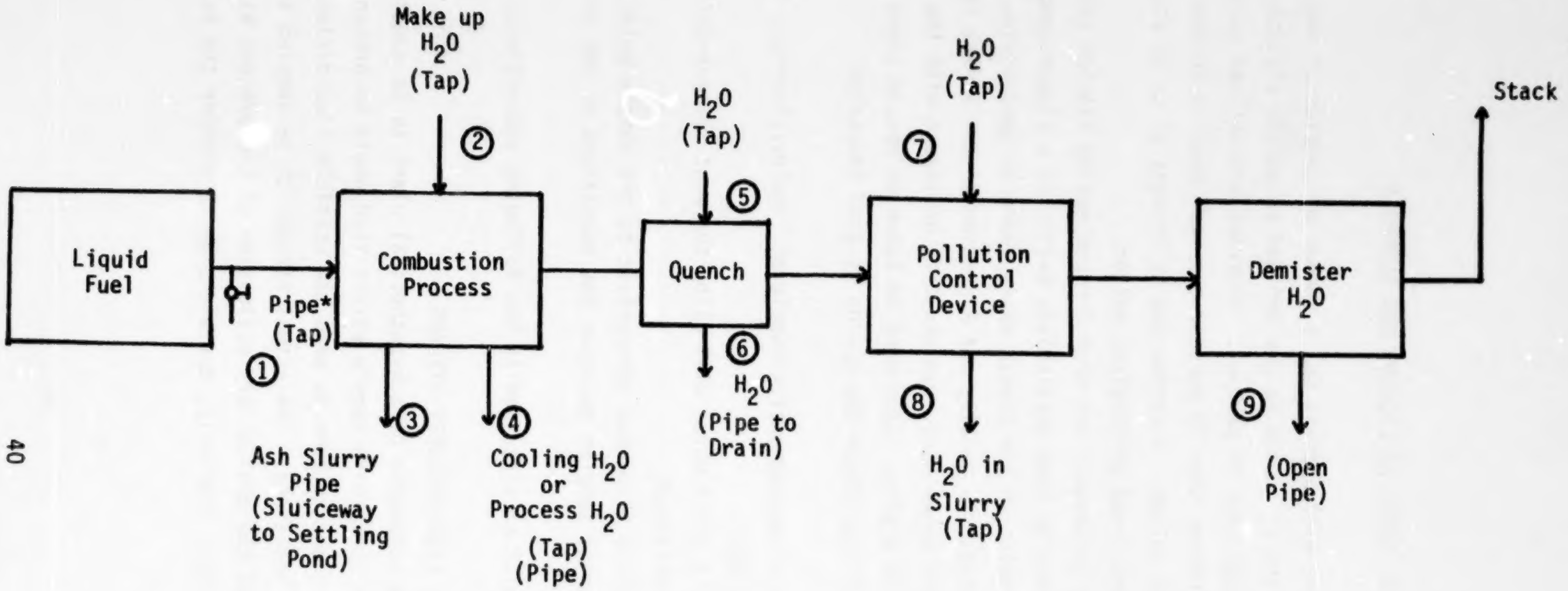

Liquid Fuel
Pipe* (Tap)
①
Make up H_2O (Tap)
②
Combustion Process
③
Ash Slurry Pipe (Sluiceway to Settling Pond)
④
Cooling H_2O or Process H_2O (Tap) (Pipe)
H_2O (Tap)
⑤
Quench
⑥
H_2O (Pipe to Drain)
H_2O (Tap)
⑦
Pollution Control Device
⑧
H_2O in Slurry (Tap)
Demister H_2O
⑨
(Open Pipe)
Stack

Figure 4-1. Hypothetical plant with liquid/slurry streams.

*Could be under pressure. Cautions should be taken as material could be hazardous.

sample locations are adequate or new ones are needed should be made at this time. It is unlikely, however, that the plant operator will provide additional sampling facilities.

There are three general locations for sampling liquids or slurry streams. These are: (1) taps or ports in a pipe, (2) as point of discharge of the pipe or channel into the combustion device or storage container, and (3) the storage tank or pond. Sampling from taps is most desirable, and sampling from storage containers is least desirable for obtaining a representative sample. Liquid/slurry streams are primarily moved by pipes rather than open channels. Most of the streams flowing in pipes will have an existing sample tap which can be used for sampling in this program. Taps will probably be used for fuel oils, liquid fuels or wastes, and scrubber water. If no sampling tap exists, a sample can be taken at the point of discharge of the pipe. For example, some liquid streams like scrubber blowdown may be sampled where they discharge into the treatment facility or sewer system. Some of the nonhazardous streams may empty directly to a storm sewer where it is combined with water runoff from the plant. It is desirable to obtain these samples prior to entry in the storm drains. The best location to sample is the point where the sample stream leaves the pipe and enters the drain as a very representative sample can be obtained and flow monitored at the same time. Also, when sampling the fuel, a sample could be obtained at the storage tank; however, it is preferable to take the sample just prior to the burner as stratification could occur in the storage tank and not all of the tank will be utilized during the test. Similarly, it is desirable to obtain a waste product prior to combination with other streams or entry to lagoons or settling ponds.

4.2 RECOMMENDED SAMPLING METHODS

The following subsection describes the recommended sampling methods for liquids and slurries. The methods presented are grab and composite grab sampling methods and are intended to provide a sample that can be used to characterize the combustion device or control device inputs and outputs in sufficient detail to fulfill the requirements of the program. More sophisticated sampling acquisition schemes, for example, integrated grab or continuous sampling schemes, are not needed to fulfill the needs of the program.

However, the methods which are recommended here are tried and proven discreet sampling techniques which are employed at selected sample points and times to yield a representative composite sample. Table 4-1 gives a brief overview of the methods presented and their application.

Since most of the streams to be sampled are contained in pipes and the objective is to obtain as representative a sample as close to the combustion process as possible, the recommended sampling procedures to be utilized will be the tap sampler, dipper, and pump sampler. Only in cases where there is no other suitable sampling procedure will the Coliwasa or weighted bottle sampler be utilized. Figure 4-1 numbered the sample points in the process, and they are reproduced in Table 4-2 along with the proper sampling technique.

If, for some reason, the preferred sample point is not available, alternate techniques should be used. Usually, this means that the only available sample source is a lagoon, pond, or tank. In this event, the weighted bottle, dipper, or Coliwasa sampler is the preferred method.

Obviously, these recommendations are not absolute, and some judgment should be used when selecting methods for the actual test site. This is one of the reasons for preparing a site-specific test plan for each facility tested. As an aid in making these judgments, each of the sampling methods is described in the sections which follow. These descriptions are not intended to be procedural guidelines, but rather to guide the selection of the proper technique when special situations are encountered.

4.3 DESCRIPTIONS OF LIQUID SAMPLING TECHNIQUES

4.3.1 Tap Sampler

Tap sampling, Figure 4-2, is the appropriate method for sampling moving liquids in pipes or ducts. Slurries in motion are sometimes sampled by tap, but this is unreliable if the solids content is much greater than 10 percent.

TABLE 4-1. SUMMARY OF LIQUID SAMPLING TECHNIQUES

Technique	Description
Tap Sampler	Appropriate for homogeneous flowing liquids in pipes or ducts.
Dipper	Surface liquid sampling device or outflow of pipe or sluiceway.
Coliwasa	Sampler which will collect liquid from standing liquids contained in drums, tanks, pits, or lagoons.
Weighted Bottle	Subsurface liquid sampling device.

TABLE 4-2. RECOMMENDED APPROACH TO SAMPLING LIQUID STREAMS

Source	Preferred Location	Preferred Sample Point	Preferred Sample Technique
1. Liquid fuel	Pipe	Tap	Tap
	Pipe	Tap	Pump
2. Ash slurry	Sluiceway	Open drain	Dipper
3. Makeup water	Pipe	Tap	Tap
4. Process/Cooling water	Pipe	Tap	Tap
5. Makeup water	Pipe	Tap	Tap
6. Quench water	Pipe	Tap	Tap
7. Makeup water	Pipe	Tap	Tap
8. Scrubber blowdown	Pipe	Tap	Tap/Pump
9. Demister blowdown	Pipe	Tap	Tap

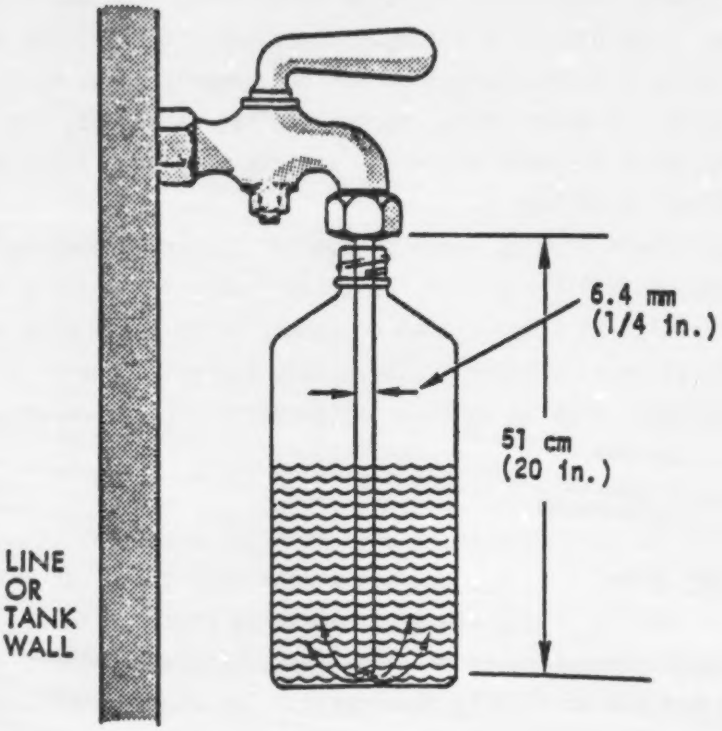

6.4 mm
(1/4 in.)
51 cm
(20 in.)
LINE
OR
TANK
WALL

Figure 4-2. Schematic of tap sampling.

To acquire a tap sample, the outlet of the valve or stopcock used for sample removal is fitted with a length of precleaned Teflon^R tubing sufficiently long to reach the bottom of the sampler container. After the Teflon^R conduit line has been placed in the sample container, the tap is opened to admit a moderate flow of liquid. The conduit line, but not the sample container, should be flushed before the sample is actually taken. Flushed material should be returned to the process.

If the sample temperature is above about 50°C, the sample should be cooled before being placed in a sample container. Cooling the sample can be affected by using a longer length of Teflon^R conduit line, coiling it, and placing it in an ice-water bath. Again, the tap is opened, and the liquid is discharged until possible sediments and gas have been flushed. Then the sample container is filled.

A moving liquid stream, known to contain particulate matter or immiscible phases, will be considered stratified. The optimum location for a sampling tap will be after a bend or constriction which will induce turbulence or at least promote mixing. Only the main pipe or stream flow should be sampled. Taps in vents or slipstreams are not recommended because solids can accumulate.

4.3.2 Dipper Sampling

The dipper or pond sampler is used to acquire samples of liquids in ponds, sluices, pits, lagoons, and tanks with open tops. It can also be used to catch samples of the end of a discharge pipe. A typical dipper sampler is shown schematically in Figure 4-3. Dipper samplers are not sold commercially but can be readily fabricated. The figure indicates that the pole should be capable of extending to 4.5 meters (15 ft). Samples as far as 3.5 meters from shore can thus be taken.

To take a sample, the dipper is inverted and lower slowly into the liquid to be sampled. At the desired sampling point, the dipper is righted, releasing trapped air and filling with sample. The dipper is then slowly removed from the pond. After removal, the outside is carefully wiped with a disposable rag or cloth, and the sample is placed into an appropriate container.

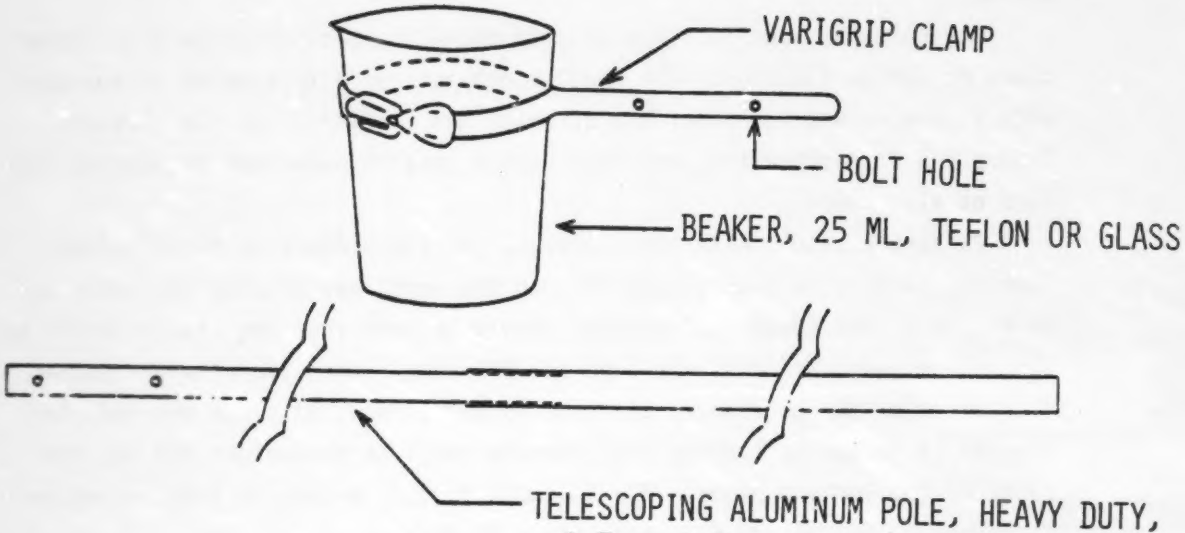

VARIGRIP CLAMP
BOLT HOLE
BEAKER, 25 ML, TEFLON OR GLASS
TELESCOPING ALUMINUM POLE, HEAVY DUTY, 2.5 TO 4.5 M (8 TO 15 FT)

Figure 4-3. Dipper sampler

4.3.3 The Coliwasa Sampler

The preferred sampling method is to use taps and end-of-pipe sampling. However, there may be circumstances under which the Coliwasa sampler should be used. The Coliwasa is employed to sample free-standing liquids and slurries contained in drums, shallow open-top tanks, pits, and similar containers. It is particularly useful for sampling wastes which consist of immiscible phases. It is easy to use, and samples may be taken quite rapidly, thereby minimizing exposure of the sampling personnel to the wastes.

Any Coliwasa used for this program should be made of glass with either glass or Teflon fittings. The sampler consists of a tube which is equipped with a closure and the other end of which has a control for the closure. Figure 4-4 is a schematic, and fabrication details have been documented (de Vera et al., 1980).

To take a sample with the Coliwasa, the end closure is first opened. Then the sampler is slowly lowered into the container holding the waste to be sampled. The speed of insertion should be such that the liquid levels on the inside and outside of the tube are the same. When the sampler reaches the bottom of the container, the tube is pushed down to close the end; the stopper is locked by turning the T-handle until it is upright and one end rests on the locking block. The Coliwasa is then withdrawn from the waste container. The outside is wiped with a disposable rag or cloth, and the sample is discharged slowly into an appropriate container.

When constructed as recommended, a Coliwasa cannot sample liquids more than 1.5 m depth. Consequently, its use will be limited to sampling drums and other shallow containers.

4.3.4 Weighted Bottle Sampler

The weighted bottle method, Figure 4-5, is used for sampling liquids or free-flowing slurries in tank trucks/cars and tanks. It can also be used for ponds, lagoons, etc., which are too deep for sampling by Coliwasa. Sufficient details for construction are given in ASTM (1975) Method D-270 and ASTM (1973) Method E-300.

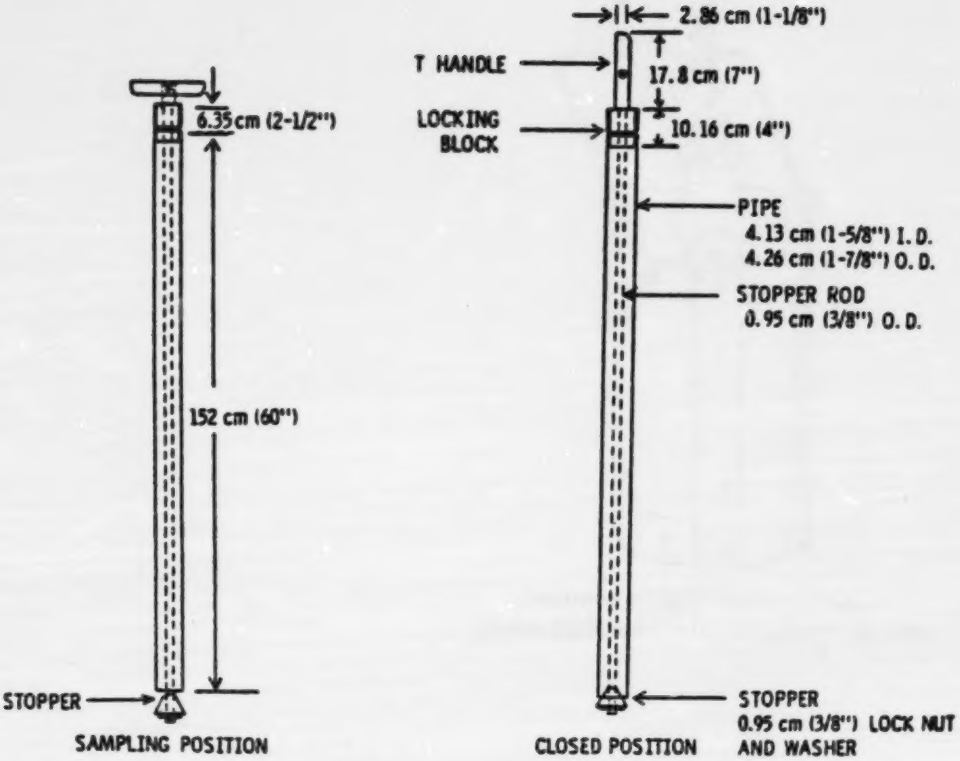

2.86 cm (1-1/8")
T HANDLE
17.8 cm (7")
6.35 cm (2-1/2")
LOCKING BLOCK
10.16 cm (4")
PIPE
4.13 cm (1-5/8") I. D.
4.26 cm (1-7/8") O. D.
STOPPER ROD
0.95 cm (3/8") O. D.
152 cm (60")
STOPPER
SAMPLING POSITION
CLOSED POSITION
STOPPER
0.95 cm (3/8") LOCK NUT
AND WASHER

Figure 4-4. Composite liquid waste sampler.
(All materials are either glass or Teflon®.)

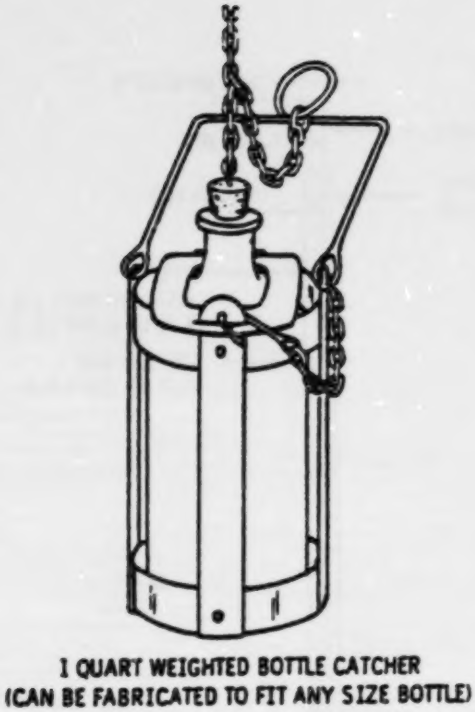

1 QUART WEIGHTED BOTTLE CATCHER
(CAN BE FABRICATED TO FIT ANY SIZE BOTTLE)

Figure 4-5. Weighted bottle sampler.
(All materials except cage and chains are either glass or Teflon®.)

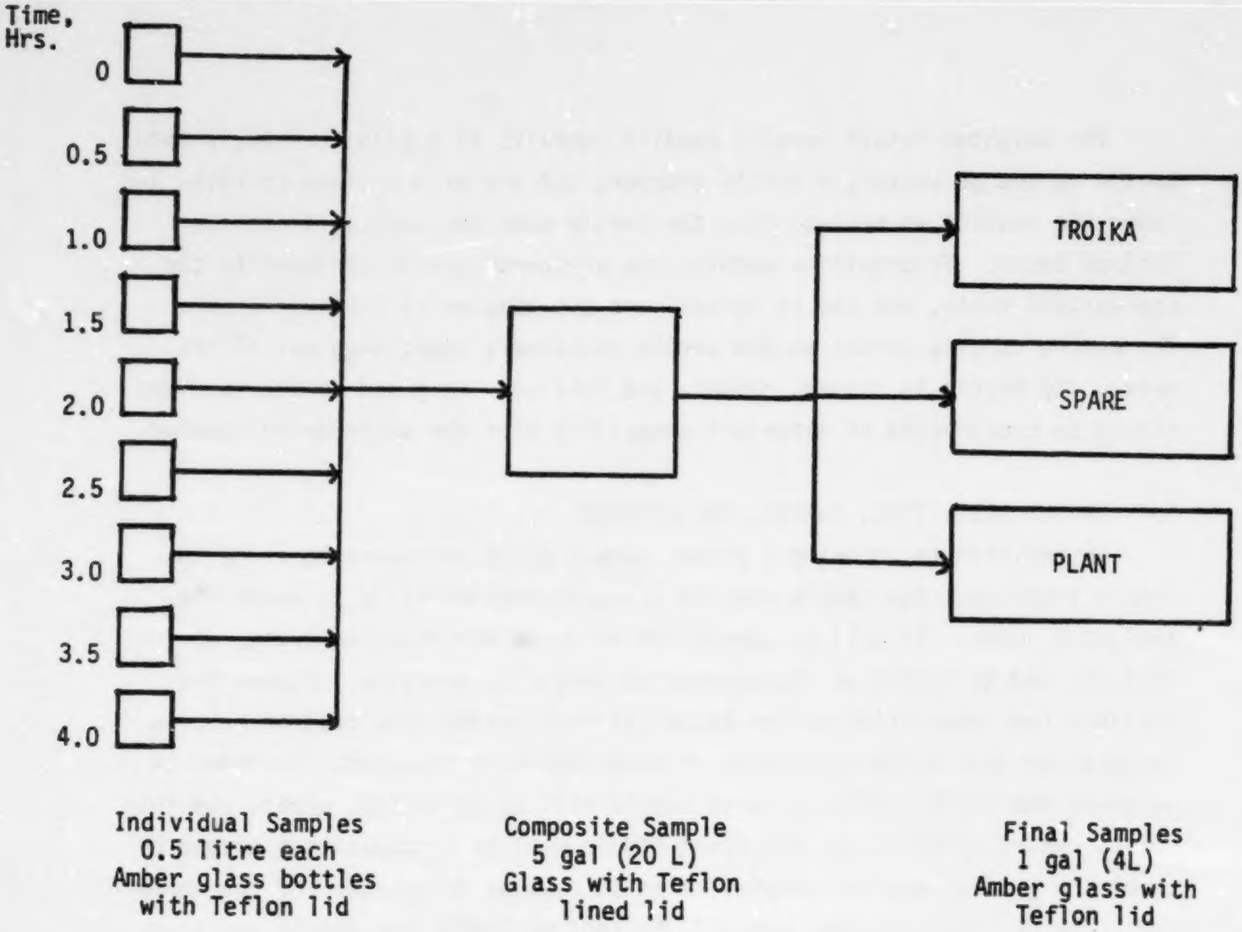
The weighted bottle sampler usually consists of a glass bottle, a metal bottle basket or sinker, a bottle stopper, and one or two lines to raise and lower the basket, as well as open the bottle when the sampler is at the desired depth. To acquire a sample, the stoppered bottle is lower to the appropriate depth, the cap is raised, and the sampler is then withdrawn. The bottle usually serves as the sample container; thus, once out of the waste, the bottle is capped, rinsed, and labeled. Weighted bottle samplers should be constructed of materials compatible with the waste being sampled.

4.4 SAMPLE SIZE, TYPE, NUMBER, AND STORAGE

In addition to choosing a proper sample point and matching it to the sample technique, the sample must be of sufficient quantity to match the analyst's needs. It will be composited so as to minimize the number of analyses and to obtain as representative sample as possible. Figure 4-6 outlines the compositing scheme to be utilized during this program. It is recommended that three replicates of each sample be prepared. In order to generate the three samples a large sample will be collected, mixed, and then split. Where appropriate, the large sample will be a composite prepared by combining several smaller samples taken at regular intervals. Of the three replicate or final samples, one will be sent to Troika for dioxin analysis, one will be given to the plant for their use, and one will be kept as a spare and used for analysis by a non-Troika lab as appropriate.

Manually prepared proportional composites (collected and mixed by hand) are recommended for this program where applicable. The total sample size will be determined by the analytical needs of the Troika. Past experience has shown this is not likely to exceed approximately 4 liters (1 gal). The size of the Troika, plant, and the spare samples will be the same and be taken from the compositing container. Therefore, the composite sample should be about 16 liters (4 gal). The material in the container should be mixed prior to splitting the composite to ensure that each sample is representative.

If the flow is steady, the sample size can be determined by dividing the number of individual samples into the total composited volume needed


Time, Hrs.
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
TROIKA
SPARE
PLANT
Individual Samples
0.5 litre each
Amber glass bottles
with Teflon lid
Composite Sample
5 gal (20 L)
Glass with Teflon
lined lid
Final Samples
1 gal (4L)
Amber glass with
Teflon lid

1. Example shown is for eight samples over four hour period. Actual number, frequency and size may vary as judged necessary by the test plan.

2. If flow is constant, equal sample volumes will be used to make the composite.

3. If flow is irregular, the individual samples will be proportioned to the flow and added. The sample size will be determined by the analytical needs of TROIKA. The spare sample and the plant sample will be of equal size.

Figure 4-6. Sample compositing scheme.

which will yield the minimum sample to be taken. If the flow is irregular, an average flow will be used to determine the average size of the discreet sample. The amount taken in each sample will be in proportion to the flow. If this information is not available until after the test, an excess individual sample will be collected, but only the composite will be specified by flow. If the flows are not known, individual samples of equal volume should be taken.

The number of liquid or slurry samples to be taken will vary from site to site based on factors such as the number of streams to be sampled, the number of separate analyses desired, and the number of remote labs involved. In the examples presented in this section, we have assumed seven distinct streams, one sample of analysis, and one remote lab (Troika). The total number of samples required for this situation is presented in Table 4-3. A similar approach can be used to determine the total number of samples to be taken at each facility. This should be done prior to arriving at the test site since sample numbers have to be assigned in advance for those sent to Troika.

4.5 CLEANING PROCEDURES

The sampling containers and sampling equipment should be cleaned prior to the test by the procedures listed in Table 4-4. The cleaned glassware will be transported to the sampling location with the Teflon^R lids tightly in place. Once the sample is introduced to the container, the lid shall be replaced and wrapped with Teflon^R tape, wrapped in cleaned foil, and transported to the analysis locations. Between sampling at the same location, no extra cleaning is necessary. When going to a new location with the same equipment, the cleaning shall consist of:

1. Removal of loose sample,
2. H_2O Rinse (x3),
3. Acetone rinse (x3) (pesticide grade),
4. Hexane rinse (x3) (pesticide grade),
5. Air dry in a clean environment, and
6. Foil wrap (hexane rinsed).

TABLE 4-3. TOTAL NUMBER OF LIQUID OR SLURRY SAMPLES REQUIRED FOR THE EXAMPLE SCENARIO
(Refer to Figure 4-1 for Sample Locations)

Source	Number of Final Samples	Number of Analyses
1. Liquid fuel	3	1
2. Ash slurry	3	1
3. Makeup water	3	1
4. Process/cooling water	3	1
5. Quench water	3	1
6. Scrubber blowdown	3	1
7. Demister blowdown	3	1
TOTAL	21	7

TABLE 4-4. PRETEST EQUIPMENT CLEANING PROCEDURE FOR SAMPLING CONTAINERS

NOTE: USE DISPOSABLE GLOVES AND ADEQUATE VENTILATION

1. Soak all glassware in hot soapy water (Alconox) 50°C or higher.
2. H_2O rinse (X3).
3. Distilled/deionized H_2O rinse (X3).
4. Chromerge rinse.
5. Distilled/deionized H_2O rinse (X3).
6. Acetone rinse (X3), (pesticide grade).
7. Hexane rinse (X3), (pesticide grade).
8. Oven dry (110°C).
9. Cap containers with Teflon lids. Foil wrap the sampling equipment.

4.6 DATA REPORTING FORMAT

The reporting format for liquid analyses will be total micrograms of TCDD per sample submitted (with the size of the analyzed sample shown). This analytical data should be combined with the process data obtained during the testing period. The sample stream flow rate should also be listed. The total TCDD emissions will be calculated by subtracting the inlet liquid stream totals from the outlet stream totals. An example data reporting format is shown in Table 4-5. Also, where appropriate the emissions should be related to the process throughput, e.g., kg emitted per ton of sludge input or kg emitted per million Btu fired. The specific method of doing this will depend on the type of process tested.

TABLE 4-5. PROPOSED RESULTS FORMAT

Site Identification ____________

Sampling Conducted by ____________

Dates from ________ to ________

Sample ID	Troika Sample No.	Stream Description (example shown)	Liquid or Slurry	Stream Flow Rate l/hr	Density, g/l	TCDD		PCDD	
						Sample size, l	Total µg	Sample size, l	Total µg
		Fuel in							
		Ash Slurry							
		Makeup Water							
		Process/ Cooling water							
		Quench Water							
		Scrubber Blowdown							
		Demister Blowdown							

5.0 SAMPLING OF SLUDGES, SOLIDS, AND SOILS

Sludges are defined as material which contains at least 20 percent moisture but do not flow. They do not move freely as a slurry would and do not mix well when stored or contained. Solids are defined as material which contains less than 20 percent moisture. Solids, dependent upon the physical state, may or may not mix well or flow well. The sampling methods utilized during this program will depend upon the physical state of the material and the sampling points of the material. As noted in Section 4.0, the objectives of the sampling program are:

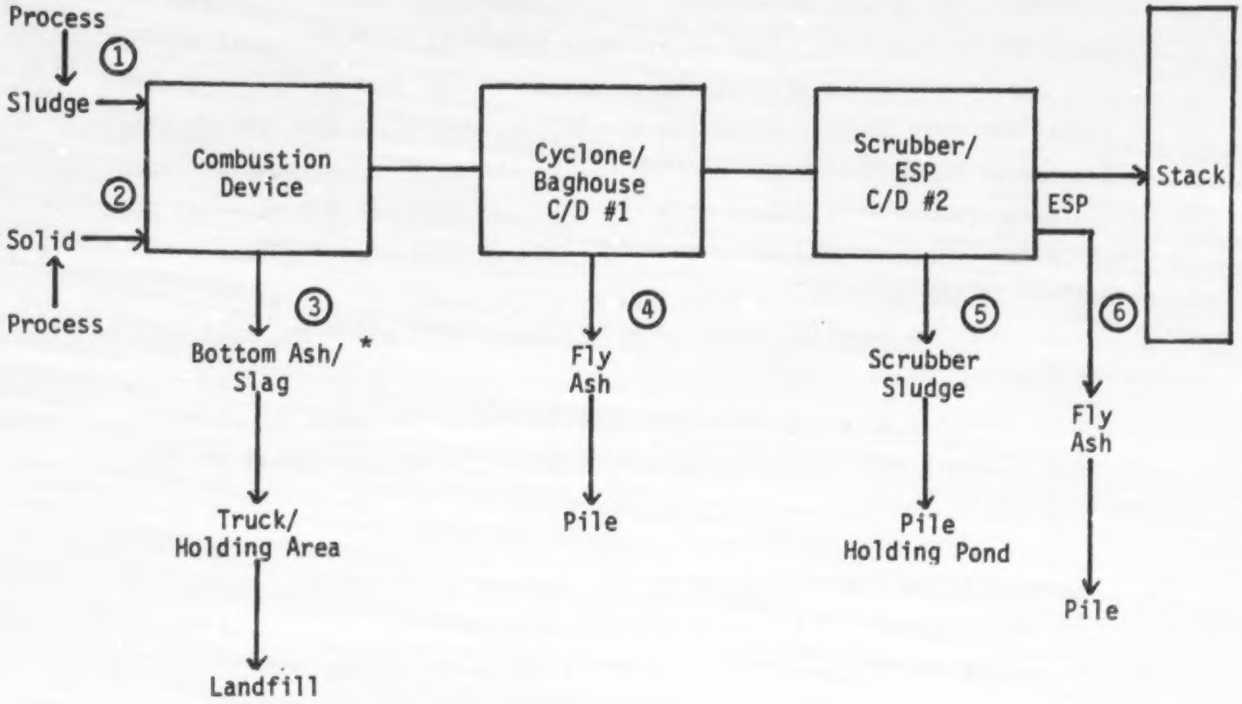
1. Choose a sampling point or points which will allow the most representative sample to be obtained.
2. Choose a sampling technique appropriate to the sampling point(s).
3. Prepare and composite the sample based on the conditions of the sample point or points.

5.1 SOURCES OF TYPICAL SLUDGE/SOLID/SOIL SAMPLES

The most typical sludge/solid streams will be bottom ash, pollution control device solids, and soils from the plant site. Also, some combustion devices may burn materials falling into these categories, for example, sewage sludge incinerators and wood fuel boilers.

Figure 5-1 illustrates a hypothetical plant to be sampled for sludges or solids. There are more sampling locations on the hypothetical plant than are present on most plants in order to illustrate all the possible sample points. The actual sample locations will be determined during the preliminary evaluation of the process or during the pretest survey. The decisions as to whether the existing sample locations are adequate or a new approach is needed will be made during the pretest survey based upon good technical judgment.

As opposed to liquids, sludges and solids are more difficult to handle and it is more difficult to obtain a sample representative of the test material during the time of the test. It is imperative that only waste streams which provide a known and definable origin be chosen for sampling.


Process
①
Sludge
②
Solid
Process
Combustion Device
③
Bottom Ash/ *
Slag
Truck/ Holding Area
Landfill
Cyclone/ Baghouse C/D #1
④
Fly Ash
Pile
Scrubber/ ESP C/D #2
⑤
Scrubber Sludge
Pile Holding Pond
ESP
⑥
Fly Ash
Pile
Stack

*This sampling location could be extremely hot. Care should be taken if bottom ash is to be taken directly upon leaving the combustion device.

Figure 5-1. Generic plant with sludge and solid sampling sites.

This is sometimes difficult as disposal of solid waste occurs during intermittent shifts and by a batch process. It is not unusual to sample for solids 24 hours after the gaseous sampling in order to provide a sample which relates to the combustion process.

Figures 5-2 through 5-4 show recommended sampling locations for some pollution control devices that may be encountered. In addition to these locations, there may be solid/sludge feed systems to the combustion device. It is desirable to obtain the samples as close as possible to the combustion or control device being evaluated. This would eliminate mixing of streams and other problems associated with unrepresentative sampling.

Soil samples should be obtained from the battery limits of the facility being tested. The area selected should be actual soil and not dirt or other material that overlays a foundation or the like. It is likely that most plants will have areas of soil that can be sampled.

5.2 RECOMMENDED SAMPLING METHODS

The choice of a sampling method is dependent upon several factors including:

1. Is the material a solid, sludge, or soil?
2. Is it free flowing, sticky, or other?
3. What kind of access is available to the material to be sampled? Open conveyor, pipe, dump truck, etc.
4. Can the material be expected to be homogeneous?

Obviously, the only approach to selecting a sampling method is to consider these and other factors and use good judgment. In this section, recommendations and guidelines are presented where one sampling method is preferable. Since the physical nature of the streams is not known, it is not possible to make firm selections as to which method is most appropriate. The methods recommended for use in this study are listed in Table 5-1 along with comments on the applicability of each to solids or sludges. Using this table, the descriptions which follow, and good judgment, the proper sampling technique can be selected.

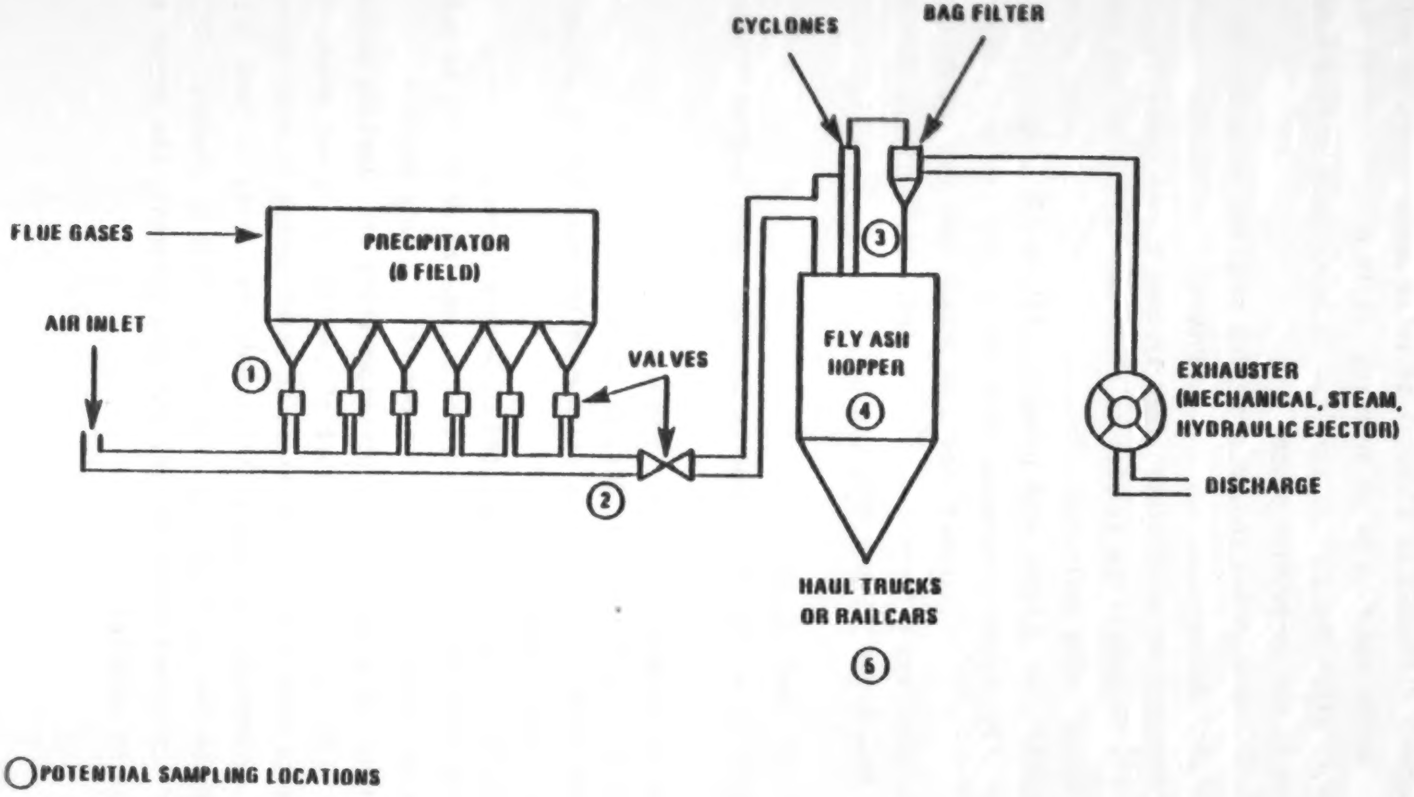

CYCLONES
BAG FILTER
FLUE GASES
PRECIPITATOR
(6 FIELD)
AIR INLET
①
VALVES
②
③
FLY ASH
HOPPER
④
EXHAUSTER
(MECHANICAL, STEAM,
HYDRAULIC EJECTOR)
DISCHARGE
HAUL TRUCKS
OR RAILCARS
⑤
○ POTENTIAL SAMPLING LOCATIONS

Figure 5-2. Vacuum ash handling system.

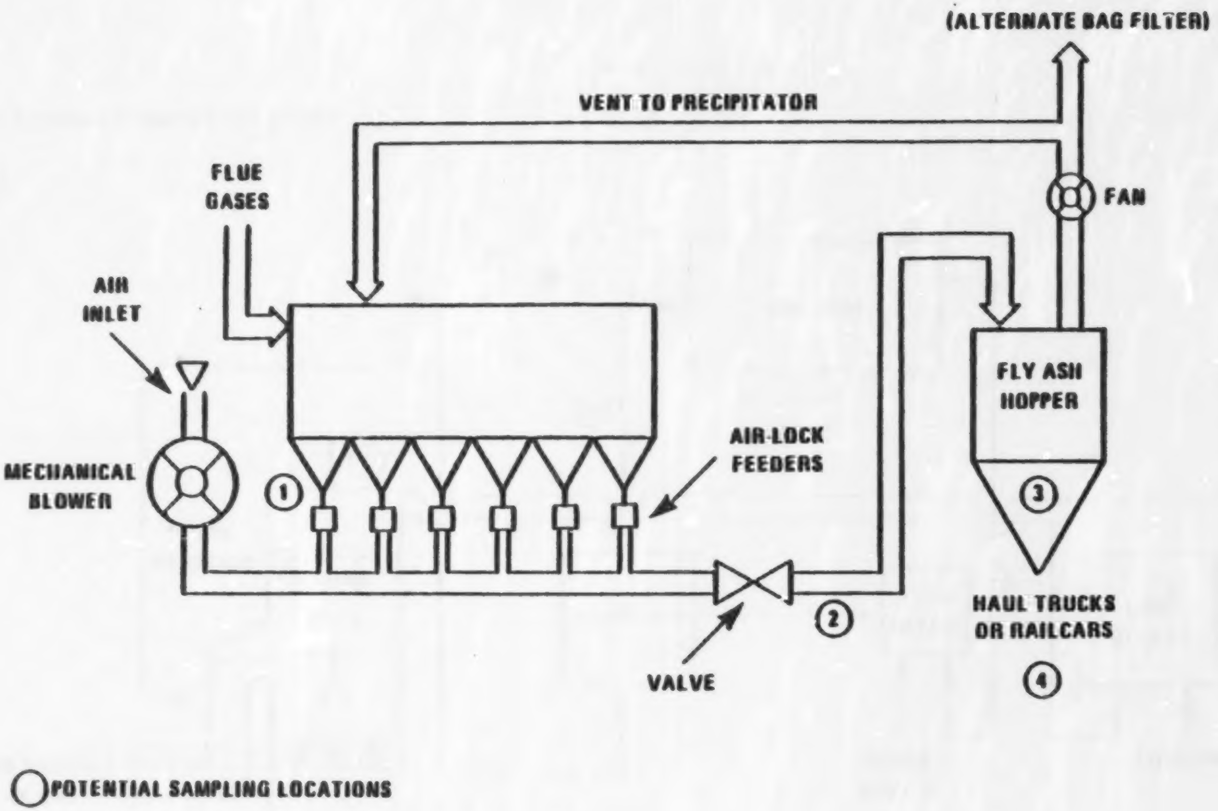

(ALTERNATE BAG FILTER)
VENT TO PRECIPITATOR
FAN
FLUE GASES
AIR INLET
MECHANICAL BLOWER
①
AIR-LOCK FEEDERS
FLY ASH HOPPER
③
VALVE
②
HAUL TRUCKS OR RAILCARS
④
○ POTENTIAL SAMPLING LOCATIONS

Figure 5-3. Air pressure ash handling system.

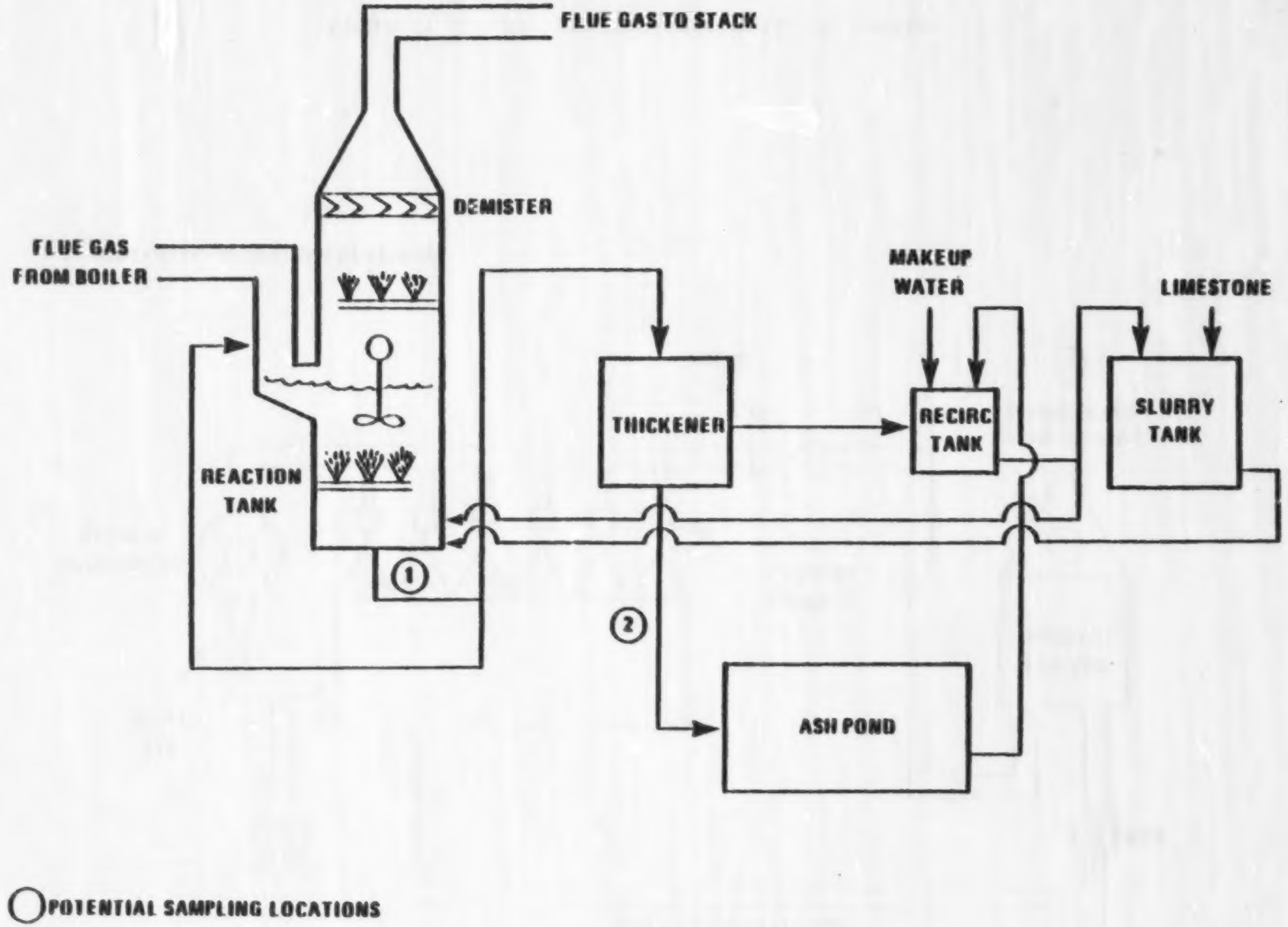

FLUE GAS TO STACK
DEMISTER
FLUE GAS
FROM BOILER
REACTION
TANK
THICKENER
MAKEUP
WATER
RECIRC
TANK
LIMESTONE
SLURRY
TANK
ASH POND
1
2
POTENTIAL SAMPLING LOCATIONS

Figure 5-4. Limestone wet scrubber.

TABLE 5-1. RECOMMENDED SAMPLING METHOD APPLICATIONS

Method	Applicable to Solids	 Sludges	 Soils	Comments
Stopped belt cut	X	X		For conveyer systems
Thief	X			For flowable, granular material
Trier	X			For granular material
Auger	(X)	X	X	For hard, solid material
Dredge	(X)	X	(X)	For sludge pits
Trough	X	X		For end of conveyer
Dipper/scoop	X	X		For end of pipe sampling
Bulb planter			X	For soils or soil-like material

X = Applicable.

5.3 DESCRIPTION OF SAMPLING TECHNIQUES

Included for each procedure is (1) a description of the scope and application of the method, (2) a summary of the method, (3) general considerations which are applicable to that method, (4) apparatus and equipment needed, and (5) sample handling provisions specific to each method. For more detailed step-by-step procedures, the sampling team will refer to the referenced standard method. Illustrations of typical classes of sampling apparatuses are provided in Figures 5-5 through 5-10. These illustrations by no means represent all possible types or configurations but are intended to aid in understanding sampling methods described in the following subsections.

5.3.1 ASTM "Stopped-Belt Cut" Method (D2234-76)

This method covers sampling of solid materials transported on conveyor belts that can be stopped for an appreciable amount of time without disrupting plant operations (i.e., several minutes). This sampling method can be applied to feed solids, dry bottom ash, char or slag, and sludge.

This is the most favorable method for obtaining a representative sample of material on a conveyor belt. With the belt stopped, a full-stream cut is obtained from the belt with a shovel and brush (for fine material). The width of the cut must be at least three times the diameter of the largest particle or 1.25 inches, whichever is greater. Also, the sides of the cut must be as nearly parallel as possible. The sample material can be placed into a storage container for transport to the lab or may be put directly into sample bottles if no other processing is required.

For measuring the width of the cut required, the diameter of the top size particles must be known (to set the minimum width allowable, as described above). A measuring tape can be used to mark off the correct width. Sample material can be removed with a shovel or with a dustpan and brush for fine-grained material. Samples can be transferred to large buckets or boxes with a large funnel or scoop. The sampling equipment must be clean and dry before use.

The sampling point(s) selected should allow complete access to either sides of the belt and should be close to a floor or platform to facilitate

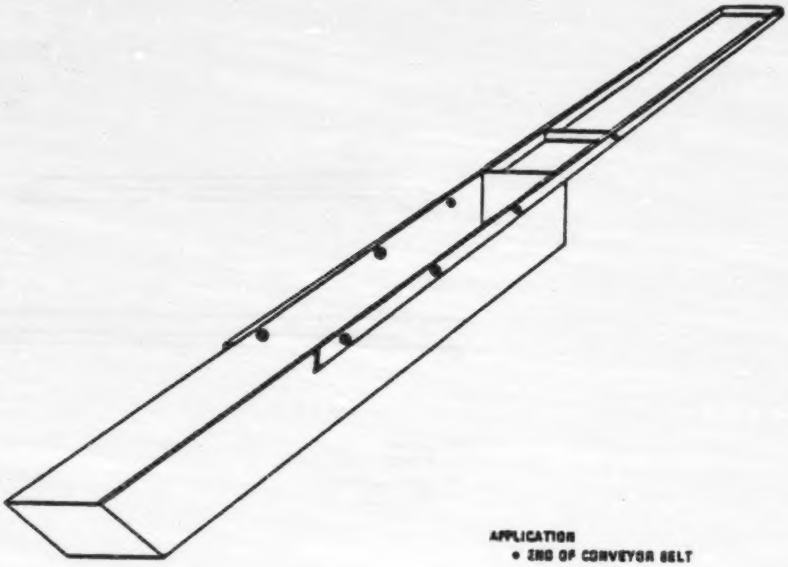

APPLICATION
• END OF CONVEYOR BELT

Figure 5-5. Sampling trough.

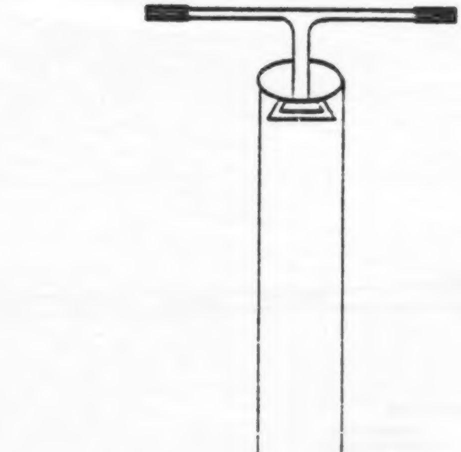

APPLICATION
• HAUL TRUCKS
• STORAGE PILES

Figure 5-6. Sample auger.

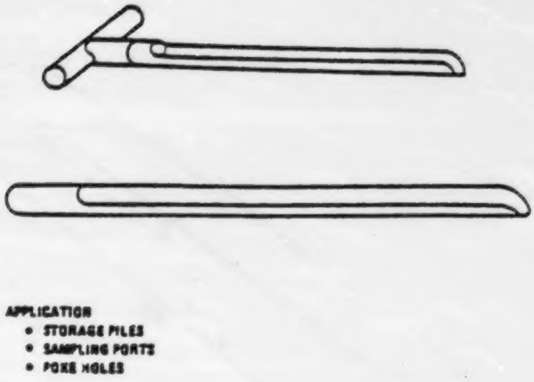

APPLICATION
• STORAGE PILES
• SAMPLING PORTS
• POKE HOLES

Figure 5-7. Sample triers.

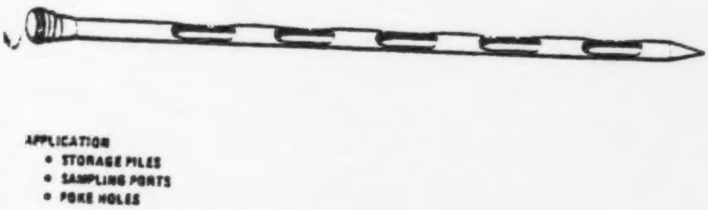
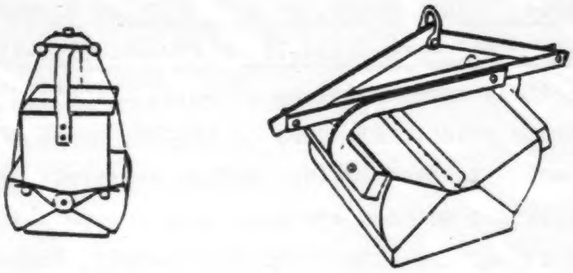
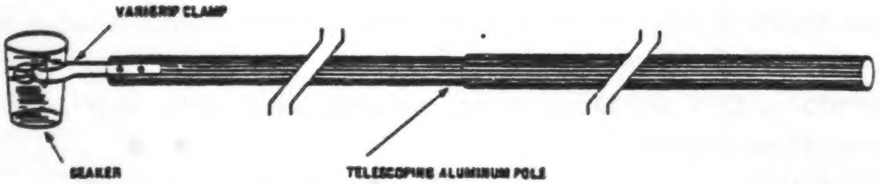

APPLICATION
• STORAGE PILES
• SAMPLING PORTS
• POKE HOLES

Figure 5-8. Sample probe or thief.



APPLICATION
- SETTLING BASINS
- THICKENERS, CLARIFIERS
- HYDROBINS

Figure 5-9. Dredge samplers (Ekman, Ponar).


VARIGRIP CLAMP
BEAKER
TELESCOPING ALUMINUM POLE

APPLICATION
- END OF PIPE SAMPLING
- THICKENERS
- SETTLING BASINS (BOTTOM)

Figure 5-10. Dipper.

moving and storing sample containers and equipment. There should be sufficient work space so that sampling personnel can shovel solids or sludge directly from the belt into containers. There should also be adequate space for personnel to stand clear of the belt if it is accidentally started.

5.3.2 Thief, Trier, Auger, or Bulb Planter Sampling of Stationary Materials (ASTM D2234-76, D2234-76, C311-77, D346-78

These methods cover sampling of solid materials that may be located in hoppers, storage piles, rail cars or trucks, or other stationary containers. The methods apply to feed solids, bottom ash/slag, fly ash, and soil.

Three possible methods are available for sampling stationary materials: D2234-76 for solids and other lumped materials, D346-78 for solids or any material in hopper cars or trucks, and C311-77 for fly ash and other granular materials (except pulverized coal).

The first method involves taking a prescribed number of increments of the material from systemically or randomly located points throughout the volume of the pile or hopper. Points that are selected systematically are preferred. The material can be shoveled from the pile, but augers or slotted pipes (thiefs) are more useful when it is necessary to remove material from the interior of a pile.

Method D346-78 is very similar to D2234-76 but also includes a useful diagram for selecting sampling points in a loaded hopper car or dump truck (see Figure 5-11). It is expected that access to certain waste materials may be restricted until after they are loaded into rail cars or trucks. Therefore, this method may be use to selected sampling points on any material so stored.

Method C311-77 involves taking grab or composite samples of granual material in bulk storage or in rail cars or trucks. Samples are to be withdrawn from the entire volume of material from "well-distributed" points over the area of storage. Samples of dust or sand-like material are probably the easiest to obtain with a thief or auger. Particular care should be taken to sample points on the outside of the pile (or surface of the container) first, since climbing on the material to obtain interior samples will disturb the outer layers.

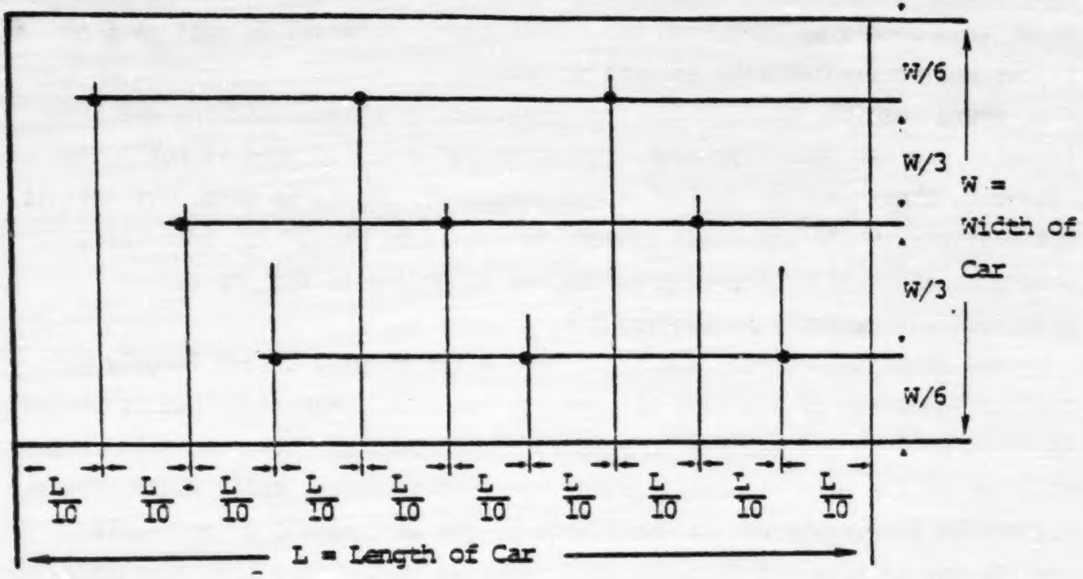

W/6
W/3
W/3
W/6
W =
Width of
Car
L/10
L/10
L/10
L/10
L/10
L/10
L/10
L/10
L/10
L/10
L = Length of Car

Figure 5-11. Example sampling grid.

Equipment needs for sampling stationary materials will be a function of the way the material is being stored. Material in piles can be sampled with shovels (small piles), borers, augers, or thiefs. A bucket or box will be needed to composite the material and take it back to the lab. Material in bins or hoppers can sometimes be drawn directly from an outlet, requiring only a sample container. Otherwise, a thief or borer (on an extension, if necessary) should be used from the access door. Material in rail cars or trucks can be sampled with shovels or borers.

Where possible the materials of construction of the sampling and transfer devices should be either glass or Teflon^R. If this is not feasible, then glass or Teflon^R lined components should be used. If this is not possible, stainless steel components should be used. All components should be thoroughly cleaned prior to use according to the procedures described subsequently in Section 5.5.

The sampling protocol for stationary material will depend largely on the configuration of the material and its location. Material that is stored in piles will be the easiest to sample, simply because access to all portions of the pile is unrestricted. In certain cases, solid waste streams may not be accessible within the plant, so the best sample of definable quality may be obtained from the haul vehicles at the time they discharge their loads at disposal sites. A systemic sampling plan that will obtain material from the entire volume of the pile (not just the surface) must be designed. Also, the size of the particles must be taken into account so that the diameter of the sampling device exceeds the top size by at least 2 1/2 times. Consideration should be made of the weathering conditions undergone by material, especially if the pile is outside. Every effort should be made to sample material that has been recently generated.

Selection of sampling points for materials in hoppers or bins may be more difficult because of access restrictions or the limitations of sampling equipment. Therefore, a representative volume may have to be drawn from the hopper outlet (ASTM C311-77).

Sampling of materials from rail cars or trucks should be similar to sampling of storage piles, except that the selection of points is constrained by the dimensions of the container. A sampling plan, similar to that outlined in ASTM D346-78, will have to be designed for each different kind of container (e.g., a dump truck vs. a 40-ft bulk trailer). Typical sample points in a rail car or other rectangular container would be selected as shown in Figure 5-11. Samples should be taken approximately 1 foot below the surface of the material in the container using an auger or similar coring-type device.

A similar approach should be taken for sampling soils. With soils, however, it will first be necessary to select a sampling site. The area selected was chosen visually as the area most likely to contain dioxin contamination. For example, soils adjacent to a waste handling area may be a good candidate. The selected area should be conceptually sectioned into grids and a composite sample made by taking material from each section and combined to make a composite. This approach is similar to that shown in Figure 5-11, rectangular rail cars.

The appropriate methods for soils are the bulb planter and auger. The bulb planter, while not illustrated here, is the common bulb planter available from garden tool suppliers. The bulb planter should be used to obtain surface samples (1" to 4" deep) while the auger should be used to obtain deeper samples. The composite, if possible, should be composed of both surface and subsurface samples.

5.3.3 Dipper/Scoop

Grab samples of sludge material may be collected if access to a sluiceway is available. The grab sample should be collected with a modified dipper. This method may also be applicable if access to an underground pipe through manholes or other access points is available.

Grab sampling with a dipper should be used for collection of sludge samples of sludge wastes are pumped from a thickener to a settling pond. With this method, randomly chosen grab samples are collected from sludge waste streams. Several samples from different locations in the sluiceway should be collected to obtain a representative cross-section.

The dipper used for grab sampling is constructed of a wide mouthed Teflon^R or glass container (1 liter volume) attached to an end of a telescoping aluminum or fiberglass pole. The dipper collects sludge samples directly from the sludge waste stream, and the sample is then transferred to an appropriately sized temporary storage container.

To take a grab sample with a dipper, the dipper is cleaned, mounted on a telescoping pole, and inserted into the stream at the desired depth with the mouth of the container down. The dipper should be turned over to an upright position, allowing the container to fill completely. The dipper can then be removed from the sludge, and the sample transferred to a temporary storage container. This process should be repeated until sufficient increments have been collected.

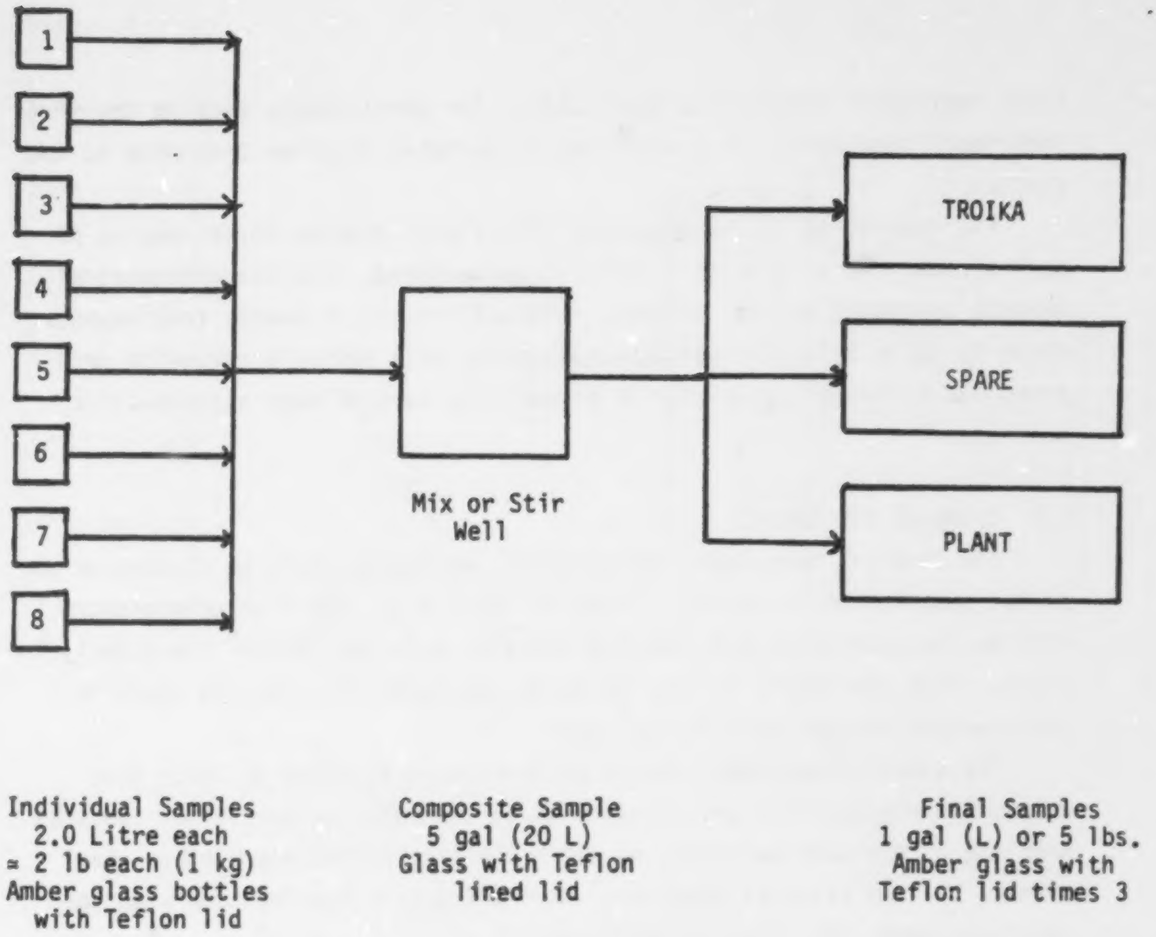
Precaution should be taken to avoid sampler loss if the waste stream is moving at a high velocity.

5.4 SAMPLE SIZE, NUMBER, AND COMPOSITING

It will be necessary to prepare composites of each stream sampled. Figure 5-12 illustrates the general procedure. The size of the individual samples should be selected so that each final, composited sample is about 4 liters or 5 pounds.

With solids, sludges, and soils, two types of compositing methods can be used. Where the solids are relatively dry, single samples can be taken at each interval and then ground, combined, and stirred, prior to splitting into the final samples. Wood chips are a good example of where this compositing technique is appropriate.

In other cases where the material is sticky, the above technique is not appropriate. Sewage sludges are an example. Mixing these samples would require a lot of transfer and contact, thereby allowing for dioxin adsorption into surfaces. For these materials, the preferred compositing technique is to add an individual sample to each of the final sample containers at every interval. In the example shown in Figure 5-11, this would involve taking the three final sample containers to the sample point, adding 0.7 liter or 0.7 lb to each and repeated at regular intervals until


1
2
3
4
5
6
7
8
Mix or Stir Well
TROIKA
SPARE
PLANT
Individual Samples
2.0 Litre each
≈ 2 lb each (1 kg)
Amber glass bottles
with Teflon lid
Composite Sample
5 gal (20 L)
Glass with Teflon
lined lid
Final Samples
1 gal (L) or 5 lbs.
Amber glass with
Teflon lid times 3

1. Example shown is for eight samples from different locations or differing time periods. Actual number, frequency and size may vary as judged by the the test plan.

Figure 5-12. Conceptual design of sample compositing method.

eight individual samples had been taken. For consistency, each of the three individual samples in the example should be taken in close proximity to one another.

The results of this compositing effort will produce three samples of each stream, one or more of which will be analyzed. For the hypothetical example presented in this section, this will result in sample requirements shown in Table 5-2. The actual requirements will probably vary with each site, and a similar table will be prepared as part of each site-specific test plan.

5.5 CLEANING PROCEDURES

The sampling containers and sampling equipment shall be cleaned prior to the test by the procedures listed in Table 5-3. The cleaned glassware will be transported to the sampling location with the Teflon^R lid tightly in place. Once the sample is introduced to the container, the lid shall be replaced and wrapped with Teflon^R tape.

The sampling equipment should be precleaned as noted in Table 5-3, wrapped in cleaned foil and transported to the sampling locations. Between sampling at the same location, no extra cleaning is necessary other than washing off the residual material. When going to a new location with the same equipment, the cleaning shall consist of:

1. Removal of excess sample,
2. H_2O rinse (X3),
3. Acetone rinse (X3) (pesticide grade),
4. Hexane rinse (X3) (pesticide grade), and
5. Air dry and wrap in foil.

5.6 REPORTING FORMAT

The reporting format for solid/sludge/soil analysis shall be total micrograms of TCDD per sample submitted (with blanks having been analyzed and subtracted from the delivered number). The final results will be expressed as μg TCDD/kg for each liter of sample and μg TCDD/hr for each sample point. The report should relate dioxin emissions on the basis of

TABLE 5-2. HYPOTHETICAL SOLID AND SLUDGE SAMPLE REQUIREMENTS

Sample #	Source	Type	# Taken	# Analysis
1	Sludge Feed	Sludge	3	1
2	Solid Feed	Solid	3	1
3	Bottom ash/slag	Solid	3	1
4	Fly ash (cyclone)	Solid	3	1
5	Scrubber sludge	Sludge	3	1
6	Fly ash (ESP)	Solid	3	1
		TOTAL	18	6

1) These figures are derived from the generic site (Figure 4-1) and are only approximate for a source containing a maximum number of liquid streams. Each site-specific test plan will incude its own requirements for samples to be taken and analyzed.

TABLE 5-3. PRETEST EQUIPMENT CLEANING PROCEDURE FOR SAMPLING CONTAINERS

NOTE: USE DISPOSABLE GLOVES AND ADEQUATE VENTILATION

1. Soak all glassware in hot soapy water (Alconox) 50°C or higher.
2. H_2O rinse (X3).
3. Distilled/deionized H_2O rinse (X3).
4. Chromerge rinse if glass, otherwise skip to 6.
5. Distilled/deionized H_2O rinse (X3).
6. Acetone rinse (X3), (pesticide grade).
7. Hexane rinse (X3), (pesticide grade).
8. Oven dry (110°C - HR).
9. Cap containers with Teflon lids. Foil wrap the sampling equipment.

plant throughput where appropriate, e.g., µg/kg sewage feed. These units would not be appropriate for soils. An example of this format is shown in Table 5-4.

TABLE 5-4. PROPOSED RESULTS FORMAT

Site Identification ____________

Sampling Conducted by ____________

Dates from ________ to ________

Sample ID	Troika Sample No.	Stream Description (example shown)	Stream Flow Rate m³/hr or kg/hr	Sludge or Solid	TCDD		PCDD	
					Sample size, m³ or kg	Total µg	Sample size, m³ or kg	Total µg
		Sludge feed						
		Solid feed						
		Bottom ash/ slag						
		Fly ash (cyclone)						
		Scrubber sludge						
		Fly ash (ESP)						

6.0 ACQUISITION OF DESIGN AND OPERATING DATA

6.1 INTRODUCTION

An important aspect of the source test effort is acquisition of operating and design data for the combustion device and control device being tested. This data will be used in the preparation of the source test report and in the evaluation and interpretation of the test results for that facility. In addition, certain operating and design data will be needed in order to evaluate the results of the entire Tier 4 sampling effort and to extrapolate the results to other combustion sources.

Specifically, we will determine if the operation is typical of the population in general by comparing the operating data with those from other units. Also, if dioxin compounds are found, these data may provide information on the effect, if any, of operating conditions on dioxin emissions.

The following subsections describe the operating data and design data that will be obtained during the test. The first presents the types of data that will be collected and is split between design and operaing data. Finally, a proposed data acquisition schedule is presented.

6.2 DESIGN AND OPERATING DATA

6.2.1 Design Data

Design information on the combustion device and associated pollution control device should be obtained as part of the source test. This information will be used to prepare the process description section of the source test report. It will also be used during the analysis of all of the Tier 4 emissions data to make comparisons and draw conclusions between sites. Some design information (stack parameters) is also needed as inputs to the modeling portion of the risk analysis.

Table 6-1 presents a list of information needs for a typical combustion source. This list was derived from the ASME protocol. Much of this data will be requested for the source during the pretest survey and will be used as inputs to the site selection process.

TABLE 6-1. DESIGN DATA NEEDS FOR COMBUSTION SOURCES

SOURCE IDENTIFICATION

1. Source Category:

    NEDS/SCC Number: ________________ Four Digit SIC Number: _ _ _ _
    Site Name: ____________________ Contact Name: ________________
    Address: ______________________ Title: ______________________
    ______________________ Phone ______________________

2. Longitude and latitude of stack.

3. Plot plan of facility showing combustion devices, control devices, fuel storage, ash storage and disposal, and plant boundaries.

4. Type/design of combustion device (e.g., multiple hearth, fluidized bed, etc.):
    ____

    Number of combustion sources at facility and designation of source tested: ______________________________

    Size of sources (MMBtu/hr, heat input, or tons fuel/waste/year:
    ____

    Fuel types used (list each fuel and percent contribution to total for source to be tested:
    1. ____________ % _____ 2. ____________ % _____ 3. ____________ % _____

5. Describe waste and process or source generating waste (e.g., primary sewage sludge treatment, black liquor from kraft process).

6. Describe waste fuel preparation method if appropriate (e.g., dewatering of sludge to X% moisture using centrifuge).

7. Describe source of chlorine or precursor contamination (e.g., chlorine in bleach plant effluent combined with black liquor).

8. Design steam production rate and conditions:
    ________________lbs/hr at ______________°F, ________psig, and
    (if saturated) ___________quality.

TABLE 6-1. DESIGN DATA NEEDS FOR COMBUSTION SOURCES (CONTINUED)

9. Waste feed properties for which unit was designed:
   - Range of heating valves ____________ to ____________ Btu/lb
   - Range of moisture contents ____________ to ____________ wt.%
   - Range of ash contents ____________ to ____________ wt %

10. Please provide a cross-sectional diagram of the facility, preferably to scale, showing the spatial relationship between the major elements of the process train, including: the waste feed system to the grate, the grate and residue removal system, shape of the furnace, primary and secondary combustion air ports, the boiler and its flue gas passages, soot blowers, major heat transfer surfaces, economizer, air pre-heater (if appropriate), air pollution control system, induced draft fan, and stack. Indicate locations of temperature detectors also.

11. Description of the boiler:

   - Supplier ____________________________
   - Furnace Volume (ft^3) ____________________
   - Firebox dimensions (ft) L __________ W __________ H __________
   - Kind of soot blowers ____________________________________
   - Soot blowing schedule (approximate times) ____________________

12. Type of combustion (e.g., excess air, starved air)

    ____

13. Overfire and underfire air distribution

   - Describe design and type of all air ports ____________________
     ____
     ____
   - Describe how total combustion air and air distribution is controlled.
     ____
     ____

14. Type of draft ____________________

    How is draft regulated? ____

15. Description of waste fuel feeding and stoking system.

   - How is feeding rate controlled? ____________________________
   - Frequency and length of feed ram stroke. ____________________

TABLE 6-1. DESIGN DATA NEEDS FOR COMBUSTION SOURCES (CONTINUED)

16. Describe the overall plant control system logic (e.g., what measurements are used as the basis for controlling firing rate?)
____
____

17. Stack height (ft) ____________
Stack diameter at top (ft) ____________

18. Describe ash handling systems (e.g., bottom ash, wet sluiced ________).

19. Type of air pollution control system ____________________

20. If Electrostatic Precipitator

- Specific collection area (ft^2/1,000 ACFM) ____________
- Design temperature at inlet (°F) ____________
- Number of independent bus sections ____________
- Number of independent bus sections in service during emission sampling ____________
- Design particulate loading at inlet ____________grains/dscf
  at outlet ____________grains/dscf
- Rapping frequency ____________

21. If Fabric Filter

- Air-to-cloth ratio (ACFM/ft^2) ____________
- Design pressure drop across bags (in., W.G.) ____________
- Design gas temperature at inlet (°F) ____________
- Total number of bags ____________
- Actual number of bags in service at time of sampling ____________
- Bag cleaning method ____________

22. Which flue gas components are regularly measured?

Oxygen ____________
Carbon monoxide ____________
Hydrocarbons ____________
Other (specify) ____________

. Is flue gas opacity regularly monitored? ____________

23. Description of existing temperature monitors.

Locations ____________
Type of temperature detector(s) ____________
Manufacturer and model number ____________

6.2.2 Operating Data

Operating data will be collected during the test and will include both the combustion device and any associated pollution control equipment.

During the pretest survey, the available facility instrumentation will be identified, and copies of operation logs will be obtained. Prior to the test, the test contractor should decide what instrument readings will be taken. For the purpose of the Tier 4 test program, the prime concern is to record combustion device and control operating parameters that potentially could affect dioxin formation. These parameters will indicate the operating status of the unit in terms of load and combustion conditions.

Examples of operating conditions that should be recorded are steam flow (10^3 lb/h), flue gas oxygen (%), flue gas CO (ppm), and flue gas temperature (°F). The values will be used to determine if the combustion device is operating at normal production levels and to compare the current operating conditions with target and design conditions. Major deviations from normal values will later be evaluated in relation to their potential impact on combustion device and control device performance and dioxin and particulate emission levels. Continuous emission monitoring data will also be recorded (see Section 3) since parts of this data are also considered operating data; e.g., flue gas flow rate.

Combustion device operating data that should be measured during a source test are plant specific. Each combustion device is usually custom designed and erected with a unique instrument and control system package. The level of instrumentation is specified by the design engineer and purchaser (plant engineering department). Based on the type of combustion device, the mode of heat recovery, the fuel and waste combusted, the size of the boiler, its cost, and the experience of the purchaser, the instrument package may range from an extremely straightforward package to one that is quite complex. In general, a minimum amount of instrumentation is necessary to safely operate the boiler, and this level of instrumentation will be present in all facilities. More complex instrument packages can include an automated computer control system that allows the source to optimize combustion and increase the overall efficiency of the operation. Typically, the instruments will, at a minimum, indicate the flows, temperatures, and pressures of major streams.

The most critical boiler parameters are recorded on continuous strip charts or circular chart records, and copies may be obtained after the stack test (at the end of the day) to provide the necessary documentation. Most facilities require the boiler operator to record key parameters at set intervals on a log sheet or in a log book. The log sheet is typically divided into the following general measurement areas: waste materials used as fuels (e.g., black liquor), auxiliary fuels, forced air, furnace drafts, gas temperatures, feedwater, steam, and miscellaneous items. These are typically recorded every 2 hours.

Table 6-2 lists the items or conditions that should be recorded during the stack test. The list is based on a typical black liquor boiler and will require adjustment for individual installations and for different fuel types.

Integrator readings should also be recorded at the beginning and ending of each test run for the following parameters:

- Waste materials used as fuels [e.g., black liquor flow (10^3 lb or gal)];
- Steam flow (lb);
- Steam used in soot blowing (lb);
- Oil flow (lb or gal); and
- Natural gas flow (10^3 ft^3).

Based on data obtained from the log, steam tables, integrator readings, and boiler design data, the following values can be calculated:

- Average steam flow for each run;
- Average waste fuel fired (10^3 lb/h) for each test run;
- Average waste composition (e.g., black liquor, solids) for each run;
- Heat input (10^6 Btu/h) to the boiler for each test run for each fuel fired (waste, oil, natural gas);
- Average boiler output (10^6 Btu/h) for each test run;

TABLE 6-2. EXAMPLE OPERATION PARAMETERS TO BE RECORDED FOR A BLACK LIQUOR RECOVERY BOILER DURING PERFORMANCE TESTS

Parameter	Variable	Units
Black liquor (for other devices, substitute appropriate parameters to monitor quantity and quality of waste fuel being fired; e.g., gallons sewage sludge and moisture content.	Liquor flow	gal/min (10^3 lb/h)
	Black liquor pressure	psig
	Gun size	None
	Number of guns	None
	Black liquor temperature	°F
	BLS to guns	%
	BL flow to ESP[a]	gal/min
	BLS to ESP[a]	%
	BL flow to evaporator[a]	gal/min (10^3 lb/h)
	BLS to evaporator[a]	%
Auxiliary fuels	Oil flow	gal/h
	Number of guns	None
	Oil pressure	psig
	Oil temperature	°F
	Natural gas rate	10^3 ft^3/h
Forced air	Primary air flow	scf/min
	Primary air pressure	in. H_2O
	Primary air temperature	°F
	Secondary air flow	scf/min
	Secondary air pressure	in. H_2O
	Secondary air temperature	°F
	Tertiary air flow	scf/min
	Tertiary air pressure	psig
	Tertiary air temperature	°F
	Total air flow	scf/min

Continued

TABLE 6-2. EXAMPLE OPERATION PARAMETERS TO BE RECORDED FOR A BLACK LIQUOR RECOVERY BOILER DURING PERFORMANCE TESTS (CONTINUED)

Parameter	Variable	Units
Furnace drafts	Furnace	in. H_2O
	Boiler inlet	in. H_2O
	Boiler outlet	in. H_2O
	Economizer outlet	in. H_2O
	ID fan inlet	in. H_2O
	Precipitator inlet	in. H_2O
Gas temperatures	Boiler outlet	°F
	Economizer outlet	°F
	Evaporator outlet	°F
	ID fan outlet	°F
	ESP inlet	°F
Feedwater	Flow	(10^3 lb/h)
	Pressure	psig
	Temperature	°F
Steam	Flow	(10^3 lb/h)
	Drum pressure	psig
	Superheater temperature	°F
Chemicals	Salt cake makeup	lb/min
Miscellaneous	Flue gas oxygen (boiler outlet)	%
	Black liquor heat value	Btu/lb BLS

[a] To be used with correction factors to calculate BLS to guns where not measured directly.

- Boiler thermal efficiency (heat output/heat input) for each test run; and
- Boiler excess air (percent).

Acquisition of combustion device operating data will depend upon available facility instrumentation. Additional process instrumentation, cannot be supplied by the test contractor. For this reason, close attention should be paid to the amount of instrumentation available at the facility during the pretest survey and the amount of data routinely recorded by the boiler operator.

In addition to monitoring and recording key operating parameters for the combustion device, it is also necessary to monitor and record operating data for the pollution control device. Anomalies in the recorded data over the period of the test should be noted in the source test report and will help interpretation of results.

The aquired control device operating data should reflect those variables which affect control device performance. These variables will vary from control device to control device. In addition, the existing instrumentation will vary from facility to facility depending upon the size and complexity of the control device. Table 6-3 indicates some variables that can be monitored for the control devices which are expected to be used at the combustion sources under study. The majority of the devices of concern are anticipated to be particulate control devices. However, some combustion sources may employ other devices, such as afterburners, etc.; and many companies have more than one device; for example, an ESP and then a scrubber. Decisions regarding which control device parameters to be monitored should be made following the pretest survey.

6.3 SCHEDULE FOR OBTAINING OPERATING DATA

The schedule for obtaining operating data will be specified in the test plan and will be based on the length of the test, plant operating schedules, and the data available from existing operating logs. The simplest method of getting this data is to make copies of the operating logs. These are recorded by the plant operators typically at 2-hour intervals. It is not likely, however, that this alone will be sufficient.

TABLE 6-3. EXAMPLE OPERATING AND MONITORING PARAMETERS FOR CONTROL DEVICES

Device	Operating Parameters
ESP	Power level (for all chambers) - Primary current - Primary voltage - Secondary current - Secondary voltage Spark rate Opacity
Scrubber	Scrubber pressure drop Scrubber liquor flow rate
Fabric filter	Pressure drop across bags Opacity
Afterburners	Fuel flow rate Inlet and outlet temperature Opacity

The recommended schedule for this program is that the data be recorded hourly. The plant operators may be willing to record instrument readings more frequently while the test is in progress. It is also likely that not all of the desired information will be contained on the operator logs. Once again, the plant operators may be able to do this during the test program. The option of having the plant increase the level and frequency of data recording should be discussed during the pretest site survey. If such arrangements are not possible, then one of the test crew personnel will be assigned the job of recording process measurements every hour.

7.0 SAFETY

Dioxins, most notably 2,3,7,8-TCDD, are toxic and can pose health hazards to humans even at low levels of exposure. For this reason, site-specific health and, if applicable, safety plans should be prepared prior to conducting sampling at Tier 4 facilities. Even if no 2,3,7,8-TCDD is suspected at a facility, other compounds may be present in several media (i.e., fuel, waste being burned, soil) and may present an exposure risk to the samplers.

A site-specific test plan will be prepared as part of each test plan. The need for attention to safety will be assessed as a result of information gathered as part of the pretest site survey. In some cases, the safety requirements may be the use of standard protective equipment without the need for the more rigorous safety procedures. The final decision on what safety requirements are necessary will be made by the Safety Officer of the test contractor after discussing the site with pretest survey personnel.

The Tier 4 test sites represent substantially less danger than most other sites in the study. The safety considerations presented here were developed from those developed for the overall dioxin assessment program. Due to the nature of the Tier 4 sites, it is anticipated that many of the procedures presented here can be relaxed or eliminated entirely. This is the purpose of the review by the Safety Officer.

7.1 SITE SAFETY

The following items represent the items that should be considered at a site where there is a strong chance of contact with dioxin or other hazardous materials. It is given here as a worst case for Tier 4 sites, since these sites are expected to have fewer exposure problems than other test sites in the program. The testing crew's Safety Officer will determine if these precautions are warranted or can be modified or eliminated. The results of this evaluation will provide the framework of the safety plan in the test plan.

1. Access - To reduce interferences with the test crew and reduce any safety risks, the number of test observers should be kept to a minimum. No personnel should be permitted near the test area without the consultation of the field crew chief. None of the test crew or observers should be allowed to wander around the site without the knowledge of the field crew chief or plant manager.

2. Physical Examinations - EPA and contractor personnel should have received a complete physical examination within the past year.

3. Personal Hygiene - No one should be permitted to eat, drink, or smoke within the site. All personnel should thoroughly wash hands and face with soap and water before leaving the site. Individuals should wash hands with soap and water before urinating. All footwear, once worn inside the site, must remain on-site until completion of the field work. At the end of each day, any disposable clothing, if used, should be removed and disposed of in 55-gallon metal drums. Individuals are expected to thoroughly shower as soon as possible after leaving the job site at the end of the day.

4. Personnel Exposure - In the event of direct skin contact with sample material, the affected area should be washed immediately with soap and water. If a decontamination is needed, there will be a person stationed in the decontamination area to assist in helping people on and off with their protective clothing.

5. Hospital - At least one non-sampling person should know the quickest route to medical facilities. The test plan should contain the phone numbers of the nearest ambulance and hospital.

6. Decontamination - If necessary, a 20 by 20 foot area located next to the site will be provided as a decontamination area. Individuals within the site should remove all their disposable clothing before exiting the area. All disposable items should be placed in large plastic bags located within this area, and the items should be properly disposed of.

In an effort to reduce the volume of contaminated trash and rinse water, team members are to make a conscious effort to minimize the amount of equipment and supplies brought into the site. It is highly advisable to use only disposable protective clothing (including booties) when sampling for dioxin in areas of suspected contamination at ppm or greater levels.

7. Disposal of Wash and Rinse Solution - All wash and rinse water should be disposed of at the end of each working day on the working site. Rinse solvents should be allowed to evaporate.

Regardless of the Safety Officer's assessment of the above procedures, minimum recommended safety requirements are the use of the following safety equipment:

- hardhat,
- safety shoes,
- eye protection,
- respirator (as needed), and
- gloves (as needed).

7.2 LABORATORY SAFETY

All dioxin analyses will be done by Troika; however, precursor analyses will be done in remote Radian laboratories. Composites of the potentially contaminated material will be done on-site. The following laboratory procedures are recommended. Here, also, these should be reviewed by the Safety Officer and amended where appropriate. The resulting list of safety procedures should appear in the test plan.

1. Protective Equipment - Use throw-away plastic gloves, apron or lab coat, safety glasses, and lab hood adequate for radioactive work.

2. Training - Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

3. Personal Hygiene - Thoroughly wash hands and forearms after each manipulation and before breaks (i.e., coffee, lunch, and shift).

4. Confinement - Isolate the work area with posted signs, segregated glassware and tools, and plastic-backed absorbent paper on benchtops.

5. Waste - Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

6. Disposal of Wastes - 2,3,7,8-TCDD decomposes above 800°C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in a good incinerator. Gross quantities

(milligrams) should be packaged securely and disposed of through commercial or governmental channels which are capable of handling high-level radioactive wastes or extremely toxic wastes. Liquids should be allowed to evaporate in a well-ventilated hood or placed inside a disposable container. Residues can then be handled as above.

7. Decontamination - Personnel should use mild soap with plenty of scrubbing action. For glassware, tools, and surfaces, Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning can also be accomplished by rinsing the Chlorothene, then washing with any detergent and water. Dishwater can be disposed to the sewer. It is prudent to minimize solvent wastes because they may require special disposal through commercial sources which are expensive.

8. Laundry - Clothing known to be contaminated should be disposed of with the precautions described under "Disposal of Wastes." Lab coats or other clothing worn in 2,3,7,8-TCDD work areas can be laundered. Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the possible hazard and trained in proper handling. The clothing can be put into a washer without contact if the launderer knows the problem. The washing machine should be run through a cycle before being used again for other clothing.

9. Wipe Tests - A useful method of determining cleanliness of work surfaces, equipment, and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by gas chromatography can achieve a limit of sensitivity of 0.1 μg per wipe. Less than 1 μg 2,3,7,8-TCDD per sample indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 μg on a wipe sample indicates an acute hazard and requires prompt cleaning before further use of the equipment or work space and also indicates that unacceptable work practices have been employed in the past.

10. Inhalation - Any procedure that may produce airborne contamination must be done with good ventilation. Gross losses to a ventilation system

should not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in case of an accident.

11. Accidents - Remove contaminated clothing immediately taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

8.0 QUALITY ASSURANCE AND CONTROL

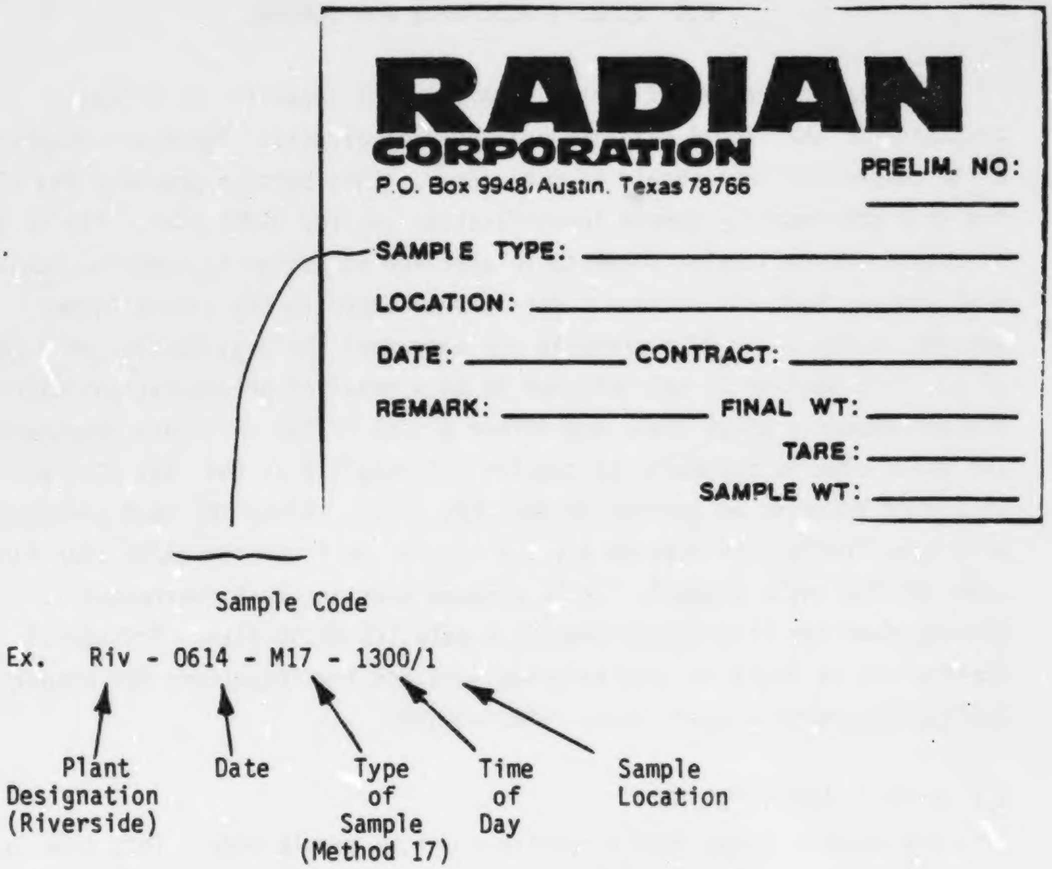
Quality assurance and control (QA/QC) is a separate and necessary component of the Tier 4 sampling and analysis efforts. There are several QA/QC components that should be considered. This section presents two of the main components - sample identification and the QA/QC plan. The section on sample identification presents an approach to assigning sampling numbers that ensures that all pertinent data are included in the sample number. The section on the QA/QC plan presents and describes the organization of a QA/QC plan. This section is not intended to be a detailed procedural guideline on how to prepare a QA/QC plan, but rather a list of the necessary components. The QA/QC plan is typically as complex and detailed as the test plan and should be prepared in advance of any test plans. Since the test procedures will vary little from site to site, a single, well written QA/QC plan can be used for the whole project. It is assumed that the test contractor is already familiar with how to prepare a detailed QA/QC plan. Procedural details can be found in Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, QAMSO-005/80.

8.1 SAMPLE IDENTIFICATION

All samples taken should receive a unique sample code. This code is separate from the identification numbers that are assigned by the Troika for their analysis. This is necessary since there may be samples that are not analyzed by Troika. In addition, there should be a constituent labeling format. This organization allows quick and accurate association of analysis results with process and other data. The label and sample code format is presented in Figure 8-1.

8.2 THE QA/QC PLAN

The U. S. Environmental Protection Agency policy stipulates that every monitoring and measurement project must have a written and approved Quality Assurance (QA) Project Plan. Sixteen essential elements must be considered and addressed in the QA Project Plan. These elements of the QA Project Plan



RADIAN CORPORATION
P.O. Box 9948, Austin, Texas 78766

PRELIM. NO: ____

SAMPLE TYPE: ____

LOCATION: ____

DATE: ____ CONTRACT: ____

REMARK: ____ FINAL WT: ____

TARE: ____

SAMPLE WT: ____

Sample Code

Ex. Riv - 0614 - M17 - 1300/1

Plant Designation (Riverside)
Date
Type of Sample (Method 17)
Time of Day
Sample Location

Figure 8-1. Example of label and sample identification code.

are listed below. The first 16 sections are the essential elements. Section 17 and 18 shown below may be used as needed. Additional sections may also be included in the QA Project Plan as appropriate.

-	Section 1	Title Page
-	Section 2	Table of Contents and Distribution
-	Section 3	Project Description
-	Section 4	Project Organization and Responsibility
-	Section 5	QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability
-	Section 6	Sampling Procedures
-	Section 7	Sample Custody
-	Section 8	Calibration Procedures and Frequency
-	Section 9	Analytical Procedures
-	Section 10	Data Reduction, Validation, and Reporting
-	Section 11	Internal Quality Control Checks
-	Section 12	Performance and System Audits
-	Section 13	Preventive Maintenance
-	Section 14	Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness
-	Section 15	Corrective Action
-	Section 16	Quality Assurance Reports to Management
-	Section 17	References
-	Section 18	Appendices

Additional details giving the contents that need to be considered for inclusion in each section is discussed below for dioxin sampling. Many of the details given are generic and should be included in any QA Project Plan. Each page of the QA Project Plan carries document control information in the upper right hand corner of the page. The information gives the section number, the Revision No. (the first draft is revision number zero), the date and the page number, usually given as "Page __ of __ pages."

Section 1 - Title Page

The title page, in addition to the title "Quality Assurance Plan for ... (Project Name)," must have the signatures of the project organization's Project Manager and Quality Assurance Official and the funding organization's Project Officer or Task Manager and QA Officer. In addition, the title page may include the project organization's name and address.

Section 2 - Table of Contents

The table of contents includes a listing of all the section numbers and their titles, the number of pages per section, the revision number, and the revision date for each section. As noted above, all the pertinent references and appendices with the title of each appendix should be listed. The table of contents also gives an official list of copy holders and will include as a minimum those who sign the title page.

Section 3 - Project Description

A general description of the project is provided. Background information gives the purpose of the test and the intended use of the data. The experimental design along with appropriate flow diagrams, equipment sketches, tables and graphs should be included. Anticipated start and completion dates for the various parts of the project test plan form part of the project description. A description of the equipment, the test design, a list of the measurements to be taken, and a description of the data analysis to be done are all components of the project description.

For sampling combustion sources, a minimum of three replicate samples is required. Simultaneous collection will be made of at least the following:

1. Auxiliary fuel,
2. Waste fuel material,
3. Ash discharge from combustion device,
4. Flue gas exiting the pollution control device -- the sampling train being developed by ASME shall be used,

5. Pollution control device(s) -- influent and effluent streams (if any), and
6. Particulate from particulate control device (if separate from scrubber.

The test design should cover the normal range of operation of the combustor and the associated emission control equipment insofar as fuel flow rate, loading, etc. Stack gases will also be monitored for O_2, CO_2, CO, and NO_x. Key operating variables of combustion device and control device also will be recorded.

Section 4 - Project Organization and Responsibility

The primary responsibility and roles of each member of the project team are summarized in a project organization chart. Where possible, persons should be named to fill the key positions. The chart shows lines of authority and communications. It is important that the QA Manager of a project reports not only to the Project Manager, but also to levels of corporate management independent of the project itself. The QA Manager of the project should be independent of the routine sampling and analytical duties and procedures. An example is shown in Figure 8-2.

Section 5 - Quality Objectives

In this section, the objectives for the data quality are listed in terms of precision, accuracy, completeness, and representativeness. Goals for precision and accuracy are based on previous experience of the project organization in the types of measurements given or from values of precision and accuracy reported in the literature from other organizations or laboratories. Sampling and analytical procedures are designed to assure representativeness of the measurements.

For combustion systems, the concentration and emission rate of a target compound (or target compounds), e.g., PCDD, is of interest. Sample sizes are selected to produce samples having concentrations greater than the expected minimum detection limit. Precision of analytical measurements with the GC/MS are probably no more than ± 30 percent when analyzing PCB's or dioxins, when they are derived from a sludge or solid waste matrix. With

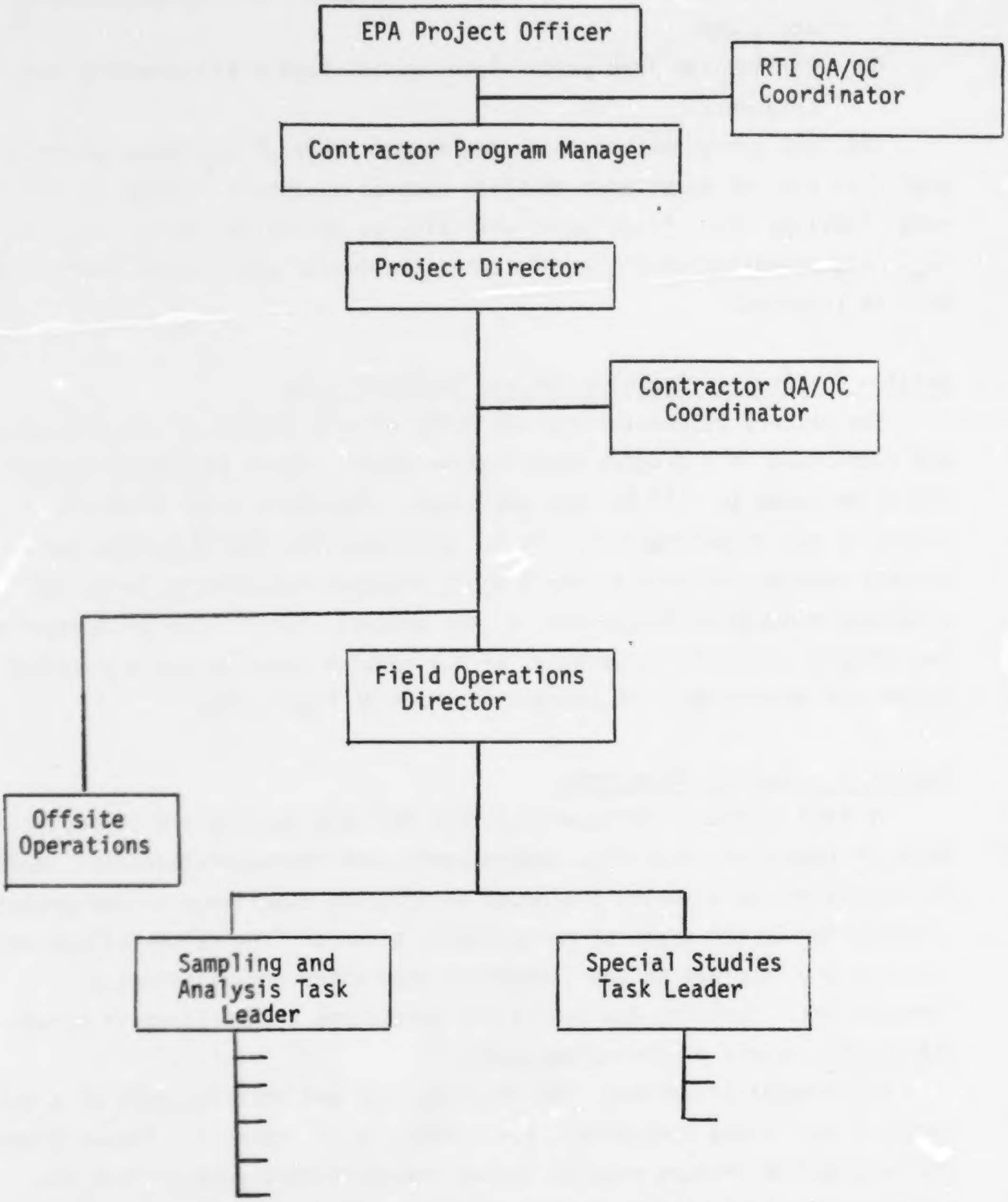

EPA Project Officer
RTI QA/QC Coordinator
Contractor Program Manager
Project Director
Contractor QA/QC Coordinator
Field Operations Director
Offsite Operations
Sampling and Analysis Task Leader
Special Studies Task Leader

Figure 8-2. Example Organization Chart.

liquids having a multicomponent matrix, precisions of ± 25 percent may be the quality objectives. For these matrices, it may not be possible to set the accuracy. For samples that are "spiked" with a dioxin, recoveries (sometimes taken as accuracy) may range from 85 to 115 percent.

Section 6 - Sampling Procedures

A detailed description of the sampling procedure for each measured parameter must be given in this section. Where standard procedures are outlined in detail elsewhere, they may be included by reference, but any deviation from a standard procedure or any nonstandard procedure must be described in detail. Charts, flow diagrams, and equipment diagrams describing sampling points, data, sample, or material flows should be given. Descriptions are given of sample containers and procedures to clean the containers and sampling equipment and sample preservation, transport, and storage methods. Section 6 also contains a description of the documentation procedures, including notebooks, data logging, sample labeling, chain-of-custody, and QA procedures for independent checks of the data logging information. Examples of all standard forms and formats should be included.

Principles of test methods and rationales for their applicability should be given. Particular attention should be focused on a consideration of the expected range of the measurement including the minimum detection limit, interferences, precision, and accuracy. A detailed description of test equipment includes a diagram and a discussion of the procedure used to prepare the equipment for sampling (i.e., cleaning procedure) and a discussion of how the sample is collected and prepared for shipment or transfer to the laboratory.

Preparation of the equipment for taking a sample includes a description of how the equipment is cleaned. If the equipment contains adsorbent beds, a description of how the bed and resin are to be cleaned and assembled is essential. Sampling equipment and sampling trains must be assembled and checked for leaks. A description is given for the operation of the sample train during the period the sample is being taken, how the sampling period is ended, and the sample is prepared for shipment. Field data sheets are prepared in advance and included in Section 6 of the QA Project Plan. If any calculations or data processing are done during the sampling phases of the project, the details of the calculations including the equations are included in this section.

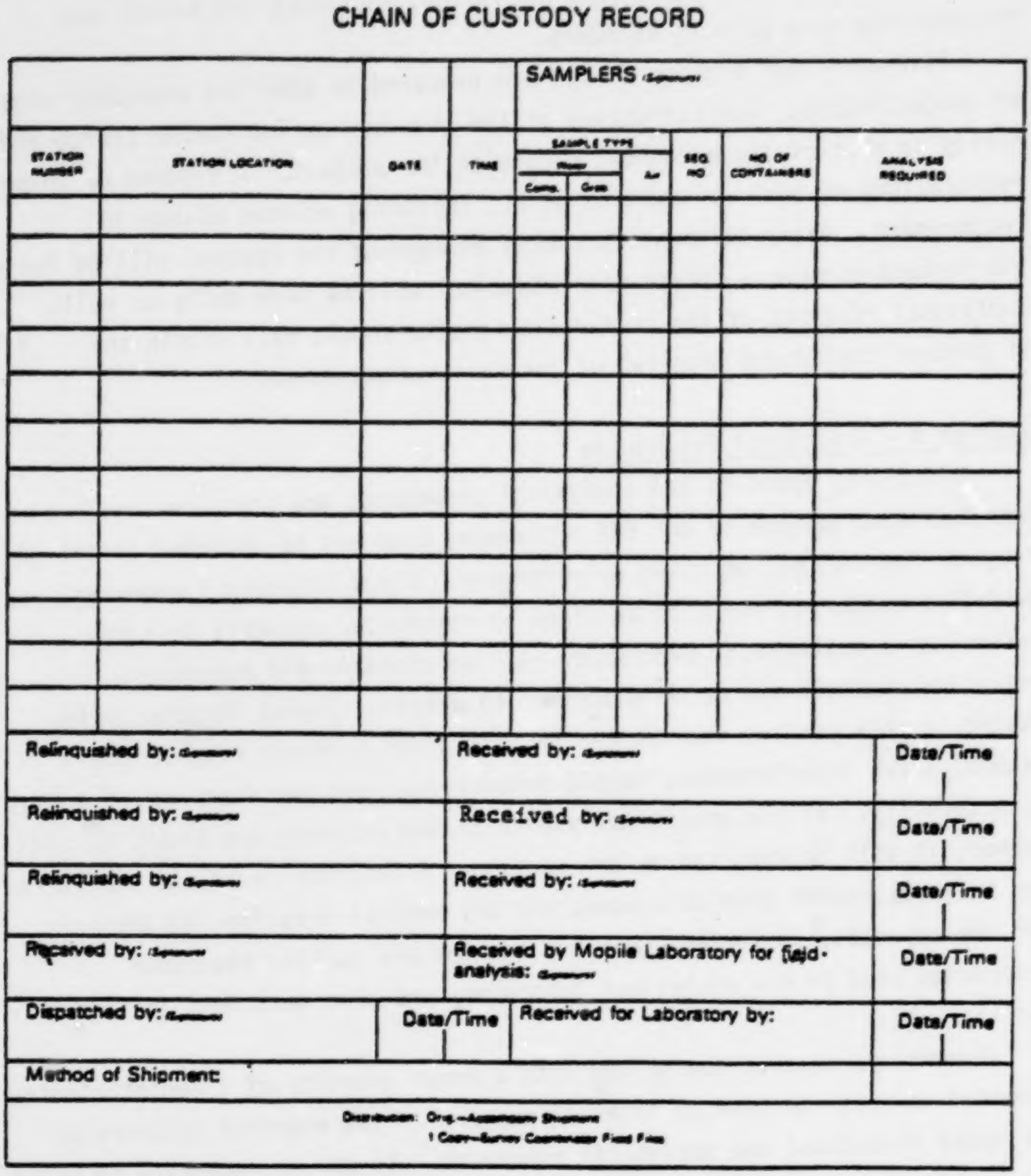
The apparatus for stack gas sampling consists of a modified EPA Method 5 train (ASME, 1984). A large (30-gram) XAD-2^R adsorbent trap is added to the Method 5 train before the normal water-filled and empty impingers. Once the XAD-2^R module is removed from the train, it is spiked in the laboratory with a labeled compound before extraction. A blank sample train may be used to assure that the train and, in particular, the adsorbent, are not being unduly contaminated by the ambient air rather than the stack gas. If used, a blank train is set up for each series of tests, and the probe and the exit of the last impinger are capped. The train remains assembled for the duration of a test. Recovery of samples from the blank train and subsequent spiking, extraction, and analysis follow the same procedure as with the regular stack sampling train.

Section 7 - Chain of Custody

An accurate written record will be maintained which can be used to trace possession of the sample from the moment of its collection until it has been analyzed. A chain-of-custody tag (Figure 8-3) will be placed on all coolers in which samples are stored and shipped. Appropriate spaces for signatures are needed when the sample is transferred from one person to another. The date and time at which the custody is transferred should be indicated on the tag.

Section 8 - Calibration Procedures and Frequency

This section requires that for each measured parameter, the standard operating procedure for the measurement is described in detail. A written description of the calibration method is required for this section, listing



CHAIN OF CUSTODY RECORD

				SAMPLERS (Signature)					
STATION NUMBER	STATION LOCATION	DATE	TIME	SAMPLE TYPE			SEQ. NO.	NO. OF CONTAINERS	ANALYSIS REQUIRED
				Water		Air			
				Comp.	Grab				

Relinquished by: (Signature)		Received by: (Signature)		Date/Time
Relinquished by: (Signature)		Received by: (Signature)		Date/Time
Relinquished by: (Signature)		Received by: (Signature)		Date/Time
Received by: (Signature)		Received by Mobile Laboratory for field analysis: (Signature)		Date/Time
Dispatched by: (Signature)	Date/Time	Received for Laboratory by:		Date/Time
Method of Shipment:				

Distribution: Orig.—Accompany Shipment
1 Copy—Survey Coordinator Field Files

Figure 8-3. Chain-of-custody tag (Versar, 1984).

also the frequency of recalibration. Any standard reference material that is to be used in the project must be listed, including its source and traceability to a primary standard.

Five-point calibration curves are prepared to span the expected range of concentration. Identification of the standard by lot number source and purity is part of the permanent record of the project. A minimum of three replications of each calibration point, including solvent blanks is recommended. Daily calibration checks throughout the project will be run at two concentrations; a "blank determination" will be made daily as well. Individual readings of the calibration checks should fall within the 95 percent confidence interval of the calibration curve.

Section 9 - Analytical Procedures

Officially approved EPA analytical procedures are used when available. Detailed descriptions of the EPA procedures need not be included in the QA Project Plan but may be cited by reference. Other standard procedures, such as ASTM procedures, may also be cited by reference, assuming that the reference is universally available. All nonstandard and developing analytical methods are to be described in detail. Topics for discussion needed in this section include the principle and applicability of the method, known interferences, sample preparation, and the range of detectability. If the analytical precision and accuracy are known for this method, it will be reported in the section. A description of the apparatus, the reagents, other chemicals used, and any special cleaning requirements for the apparatus is needed. Quality control and quality assurance procedures used in the analytical laboratory are also described in this section.

Generally, samples are spiked with a known quantity of a noninterfering compound in order to have an interval measure of the expected recovery of the spike throughout the analytical procedure. It may be necessary to spike the sample at more than one point in the analysis in order to check on the validity and the integrity of each step in the analytical procedure. Quality control checks are generally conducted to monitor the recovery of the spike with each sample in order to assure that the analytical procedure is in control. Interval standard spikes may also be used at the point of analysis (e.g., injection of the sample into a GC/FID), and quality control charts again monitor the "control" at the time of injection.

Part of the experimental design includes the specification of the number of replications that are needed to determine the precision of the measurements. The description of the method for determining the accuracy of the measurements is included in this section. A common analytical quality control procedure is the daily analysis of a calibration standard. Frequently, a "blank" is run as a daily calibration check. In this case, a control chart is maintained should the blank produce a signal so that a check can be kept on instrument drift or sample carryover from one analysis to another.

Section 10. Data Reduction, Validation, and Reporting

The data reduction scheme for each major measured parameter is described in this section. The description includes all the equations used to calculate each reported parameter. The methods used to treat outliers and the criteria used to validate the data are described. It may be desirable to present a graphical data flow scheme from collection of the data through storage of the validated compositions.

Separate descriptions are generally needed for data validation procedures for field and laboratory operations.

Section 11 - Internal Quality Control Checks

All of the quality control checks applied in the field and laboratory operations are described in this section. The equations used to drive the quality control checks and the criteria used to determine whether the procedure is in control are described. The criteria used to check the control of any measurement are included (e.g., the acceptable pressure change for a leak-check determination).

When a daily calibration check is made, either a quality control chart is maintained or a confidence interval is established in advance in order to specify the acceptability of the calibration check reading. In case the calibration check fails the acceptability limits, the procedure used to correct such an occurrence is described.

Section 12 - Performance and System Audits

Internal and external procedures to measure the overall system performance are described in this section. It is necessary not only to audit the measurements but also the record-keeping activities of the personnel on the project periodically throughout the course of the project.

Section 13 - Preventive Maintenance

In the QA Project Plan, a schedule of Preventive maintenance tasks is given before and during the duration of the project. A list of critical spare parts needed for both field and laboratory operations is listed in this section. The concern addressed in this section is the effort expended to minimize any possible downtime because of failure of instrument or apparatus.

Section 14 - Procedures Used to Assess Data Precision, Accuracy, and Completeness

For each measured parameter, the QA Project Plan describes the procedures used to assess the precision, accuracy, and completeness of the data. This section describes all the statistical and other mathematical methods to describe the calculations of central tendency, measures of variability (for precision), and tests of significance. Calibration data most frequently fit a linear model. Equations used to fit the calibration curve are generally derived by the method of least squares. It is then possible to derive equations for the confidence interval for any particular calibration measurement. The 95 percent confidence interval is most frequently used although the 99 percent interval may be more appropriate. Equations may also be given to test the calibration curve for linearity.

Tables and equations required to test data for outliers may be included in this section. Should an analysis of variance be appropriate for the data, the models and equations for these operations are included in this section.

When using control charts for routine operations, analyses, etc., the equations used to derive the upper and lower control limits are given, along with the criteria used to detect control.

Section 15 - Corrective Action

Corrective action procedures include tabulations of the predetermined limits beyond which corrective action is required. The type of corrective action and the person who "initiates" the corrective action must be identified. The corrective action taken must be noted in the permanent record of the project, and the person who endorses and approves the action must be noted in the QA Project Plan.

Corrective action may be initiated as a result of:

- Performance audits,
- System audits,
- Laboratory/interfield comparison studies,
- Out-of-control condition on a quality control chart, or
- Other QC control conditions defined in the QA Project Plan.

Since a corrective action cannot be anticipated for every cause of corrective action, they frequently involve consultation for each case with the Program Manager, Laboratory Manager, and/or the Quality Assurance Officer.

Section 16 - Quality Assurance Reports to Management

QA Project Plans identify minimum report requirements for the project; e.g., weekly, monthly, quarterly, etc. Part of these reports should identify at least the following:

- Periodic assessment of measurement of data accuracy, precision, and completeness;
- Results of performance audits;
- Results of system audits; and
- Significant QA problems and recommended solutions.

In addition, any time a critical QA problem arises, it should be brought to the attention of the sponsoring authority, along with the recommended solution. A section of the final report of any project must summarize the QA actions and results for the entire project.

9.0 SITE SPECIFIC TEST PLAN OUTLINE

It is standard practice to prepare a test plan prior to conducting any source test, and such a plan will be a component of this program. The test plan is specific to a particular site and contains detailed information on how to set up the equipment, conduct the test, maintain records, and reduce the data. It also contains details on what QA/QC procedures will be included with the tests. The purpose of the test plan is two-fold: (1) as a reference for the field test team, and (2) to ensure that all details are thought out in advance. It also gives the EPA an opportunity to verify that the testing approach is consistent with the program's objectives. It is intended to be used in conjunction with the QA/QC Project Plan.

Several sites will be tested, and it will be necessary to prepare a test plan for each. Since the test objectives and approach are the same for each site, the test plans will be very similar. This section presents a generic test plan that includes all of the standard items and procedures. The details of what will be necessary to use the existing stack port will be different for each site; however, the use of this outline keeps the documents consistent from test to test and allows them to be prepared quickly after the pretest site survey.

Figure 9-1 presents a detailed outline for the test plan. It is important that the test plan contain as much detail as possible. This includes detailed diagrams of where and how to set up equipment, data recording forms, equations used to reduce the data, etc. This will avoid repetitive work later on. It is recommended that the test plan be prepared during the initial screening phases of the project so that it can be reviewed and approved prior to the field operations. This will allow any deficiencies to be detected and corrected.

- 1.0 INTRODUCTION
- 2.0 SUMMARY
- 3.0 PROCESS DESCRIPTION
- 4.0 TESTING PROCEDURES
  - 4.1 DESCRIPTION OF SAMPLING LOCATIONS
    - 4.1.1 Gaseous Samples
      - 4.1.1.1 Precombustion Air
      - 4.1.1.2 Combustion Device Outlet
      - 4.1.1.3 Pollution Control Device Outlet
      - 4.1.1.4 Feed Streams
        - Fuels
        - Waste streams
    - 4.1.2 Liquid and Slurry Samples
      - 4.1.2.1 Feed Streams
        - Fuels
        - Wastes
      - 4.1.2.2 Make-up Water
      - 4.1.2.3 Sluiced Ash
      - 4.1.2.4 Quench/Cooling Water Blowdown
      - 4.1.2.5 Scrubber Blowdown
      - 4.1.2.6 Demister Drain
    - 4.1.3 Solid and Sludge Samples
      - 4.1.3.1 Feed Streams
        - Fuels
        - Wastes
      - 4.1.3.2 Ash Hopper
      - 4.1.3.3 Soils
  - 4.2 SAMPLING PROCEDURES
    - 4.2.1 Gases
      - 4.2.1.1 CEM Sampling Train
      - 4.2.1.2 Manual Methods
        - Flow rate
        - Moisture
        - Particulates
    - 4.2.2 Liquids and Slurries (include only methods appropriate to the site)
      - 4.2.2.1 Tap
      - 4.2.2.2 Dipper
      - 4.2.2.3 Coliwasa
      - 4.2.2.4 Weighted Bottle

Figure 9-1. Recommended outline of a site specific test plan for Tier 4.

4.2.3 Solids and Sludges (include only methods appropriate to the site)
4.2.3.1 Thief
4.2.3.2 Trier
4.2.3.3 Shovel
4.2.3.4 Auger

4.3 SAMPLE PRESERVATION AND ANALYTICAL PROCEDURES
4.3.1 Sample Preservation
4.3.3.1 Samples for Remote Laboratory Analysis
4.3.3.2 Samples for Archive Purposes
4.3.2 Analytical Procedures
4.3.2.1 Gases
- CEM
- Manual Methods

4.3.2.2 Liquids and Slurries
4.3.2.3 Solids and Sludges

4.4 QUALITY ASSURANCE AND QUALITY CONTROL
4.4.1 Calibration Procedures
4.4.2 Documentation for Audit Control
4.4.3 Internal Quality Control Checks

5.0 FIELD TESTING SCHEDULE

5.1 GENERAL SCHEDULE

5.2 SPECIFIC SCHEDULED ACTIVITIES
5.2.1 Equipment Set-up
5.2.2 Daily Activities During Source Test
5.2.3 Equipment Take-down

5.3 PLANT SPECIFIC SCHEDULE AND DATA NEEDS

6.0 DATA HANDLING

6.1 GENERAL PROCEDURES (FIELD LOG BOOKS, ETC.)

6.2 WORK-UP OF CEM DATA

6.3 VOLUMETRIC FLOW RATE DETERMINATION

6.4 MOLECULAR WEIGHT DETERMINATION

6.5 MOISTURE DETERMINATION

Figure 9-1. Continued.

7.0 SAFETY

- 6.6 PARTICULATE LOADING DETERMINATION
- 6.7 PROCESS DATA REDUCTION
- 7.1 SITE CONSIDERATIONS
- 7.2 SAFETY PROCEDURES WHILE SAMPLING
- 7.3 LABORATORY SAFETY
- 7.4 SAFETY INFORMATION FORM
  - 7.4.1 Emergency Telephone Numbers
  - 7.4.2 Basic Safety Equipment Checklist
  - 7.4.3 Standard Procedures

Figure 9-1. Concluded.

APPENDIX A

DRAFT ASME SAMPLING PROTOCOL

"SAMPLING FOR THE DETERMINATION OF CHLORINATED ORGANIC COMPOUNDS IN STACK EMISISIONS"

DRAFT, OCTOBER 1984

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SAMPLING FOR THE DETERMINATION OF CHLORINATED ORGANIC COMPOUNDS IN STACK EMISSIONS

1. PRINCIPLE AND APPLICABILITY

1.1 Principle: Stack gases that may contain chlorinated organic compounds are withdrawn from the stack using a sampling train. The analyte is collected in the sampling train. The compounds of interest are determined by solvent extraction followed by gas chromatography/mass spectroscopy (GC/MS).

1.2 Applicability: This method is applicable for the determination of chlorinated organic compounds in stack emissions. The sampling train is so designed that only the total amount of each chlorinated organic compound in the stack emissions may be determined. To date, no studies have been performed to demonstrate that the particulate and/or gaseous chlorinated organic compounds collected in separate parts of the sampling train accurately describes the actual partition of each in the stack emissions. If separate parts of the sampling train are analyzed separately, the data should be included and so noted as in Section 2 below. The sampling shall be conducted by competent personnel experienced with this test procedure and cognizant of intricacies of the operation of the prescribed sampling train and constraints of the analytical techniques for chlorinated organic compounds, especially PCDDs and PCDFs.

Note: This method assumes that the XAD-2 resin collects all of the compounds of interest from the stack emissions. Since the method at the present time has not been validated in the presence of all the other components present (HCl, high organic load) in the stack emission, it is recommended that appropriate quality control (QC) steps be employed until such validation has been completed. These QC steps may include the use of a backup resin trap or the addition of a representative labeled standard (distinguishable from the internal standard used for quantitation) to the filter and/or the XAD-2 in the field prior to the start of sampling. These steps will provide information on possible breakthrough of the compounds of interest.

2. REPORTABILITY

Recognizing that modification of the method may be required for specific applications, the final report of a test where changes are made shall include: (1) the exact modification; (2) the rationale for the modification; and (3) an estimate of the effect the modification will produce on the data.

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3. RANGE OF MINIMUM DETECTABLE STACK GAS CONCENTRATION

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method sensitivity is also highly dependent on the volume of stack gas sampled and the detection limit of the analytical finish. The user shall determine for their system the minimum detectable stack gas concentration for the chlorinated organic compounds of interest. The minimum detectable stack gas concentration should generally be in the ng/m^3 or lower range.

4. INTERFERENCES

Organic compounds other than the compounds of interest may interfere with the analysis. Appropriate sample clean-up steps shall be performed. Through all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than polytetrafluorethylene (TFE®). Adhesives should not be used to hold TFE® liners on lids (but, if necessary, appropriate blanks must be run), and lubricating and sealing greases must not be used on the sampling train.

5. PRECISION AND ACCURACY

Precision and accuracy measurements have not yet been made on PCDD and PCDF using this method. These measurements are needed. However, recovery efficiencies for source samples spiked with compounds have ranged from 70 to 120%.[1,3]

6. SAMPLING RUNS, TIME, AND VOLUME

6.1 Sampling Runs: The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

6.2 Sampling Time: The sampling time must be of sufficient length to provide coverage of the average operating conditions of the source. However, this shall not be less than three hours (3).

6.3 Sample Volume: The sampling volume must be sufficient to provide the required amount of analyte to meet both the MDL of the analytical finish and the allowable stack emissions. It may be calculated using the following formula:

$$\text{Sample Volume} = A \times \frac{100}{B} \times \frac{100}{C} \times \frac{1}{D}$$

A = The analytical MDL in ng
B = Percent (%) of the sample required per analytical finish run
C = The sample recovery (%)

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D = The allowable stack emissions (ng/m^3)

Example: A = 0.050 ng; B = 10%; C = 50%; and D = 1 ng/m^3

$$SV = 0.05 \times \frac{100}{10} \times \frac{100}{50} \times \frac{1}{1} = 1m^3$$

7. APPARATUS

Sampling Train: The train consists of nozzle, probe, heated particulate filter, and sorbent module followed by four impingers (Fig. 1). Provision is made for the addition of (1) a cyclone in the heated filter box when testing sources emitting high concentrations of particulate matter, (2) a large water trap between the heated filter and the sorbent module for stack gases with high moisture content, and (3) additional impingers following the sorbent module. If one of the options is utilized, the option used shall be detailed in the report. The train may be constructed by adaption of an EPA Method 5 train. Descriptions of the sampling train components are contained in the following sections.

7.1.1 Nozzle

The nozzle shall be made to the specifications of EPA Method 5. The nozzle may be made of nickel plated stainless steel, quartz, or borosilicate glass.

7.1.2 Probe

The probe shall be lined or made of TFE®, borosilicate, or quartz glass. The liner or probe extends past the retaining nut into the stack. A temperature controlled jacket provides protection of the liner or probe. The liner or probe shall be equipped with a connecting fitting that is capable of forming a leak-free, vacuum-tight connection without sealing greases.

7.1.3 Sample Transfer Lines (optional)

The sample transfer lines, if needed, shall be heat traced, heavy walled TFE® (1.3 cm [1/2 in.] O.D. x 0.3 cm [1/8 in.] wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line should be as short as possible and must be maintained at 120°C.

7.1.4 Filter Holder

Borosilicate glass, with a glass frit filter support and a glass-to-glass seal or TFE® gasket. A rubber gasket shall not be used. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

[illegible]

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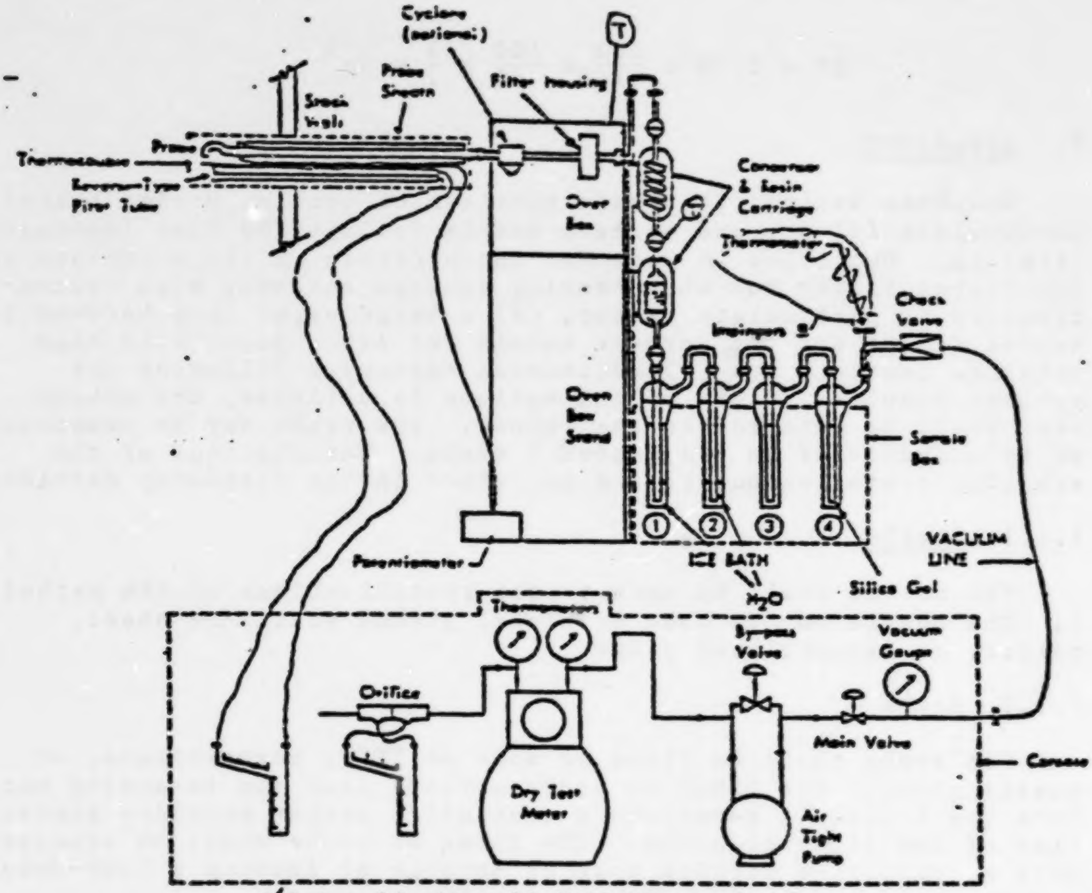
Cyclone (optional)
T
Probe Sheath
Filter housing
Stack Wall
Probe
Thermocouple
Reverse-Type Pitot Tube
Oven Box
Condenser & Resin Cartridge
Thermometer
Check Valve
Impingers a/
Oven Box Stand
Sample Box
1
2
3
4
Potentiometer
ICE BATH
H_2O
Silica Gel
VACUUM LINE
Thermometers
By-pass Valve
Vacuum Gauge
Orifice
Main Valve
Console
Dry Test Meter
Air Tight Pump

a/ Impingers ~~1, 2 and 4~~ are of the Modified Greenburg-Smith Type
~~Impinger 3 is of the Greenburg-Smith Design~~
Impinger 1 and 2 Contain 100 ml Water
Impinger 3 Empty
Impinger 4 Contains 200-300 Gram Silica Gel.
Impinger 1 is the hexane-rinsed back-up to the resin cartridge

add

Fig. 1 Modified EPA Method 5 Train for Organics Sampling
Source: Methods Manual Sampling and Analysis Procedures for Assessing Organics Emissions from Stationery Combustion Sources in Exposure Evaluation Division Studies, U.S. Environmental Protection Agency Report No. EPA-560-82-014 (January 1982).

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7.1.5 Cyclone in Filter Box (optional)

The cyclone shall be constructed of borosilicate glass with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases.

7.1.6 Filter Heating System

The heating system must be capable of maintaining a temperature around the filter holder (and cyclone, if used) during sampling of 120±14°C (248±25°F). A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

7.1.7 Solid Sorbent Module

Amberlite XAD-2® resin (XAD-2), confined in a trap, shall be used as the sorbent. The sorbent module shall be made of glass with connecting fittings that are able to form leak-free, vacuum-tight seals without use of sealant greases (Figs. 2 and 3). The XAD-2 trap must be in a vertical position. It is preceded by a coil-type condenser, also oriented vertically, with circulating cold water. Gas entering the sorbent module must be maintained at ≤20°C (68°F). Gas temperature shall be monitored by a thermocouple placed either at the inlet or exit of the sorbent trap. The sorbent bed must be firmly packed and secured in place to prevent settling or channeling during sample collection. Ground glass caps (or equivalent) must be provided to seal the sorbent-filled trap both prior to and following sampling. All sorbent modules must be maintained in the vertical position during sampling.

7.1.8 Impingers

Four or more impingers with connecting fittings able to form leak-free, vacuum-tight seals without sealant greases when connected together, shall be used. All impingers are of the Greenburg-Smith design modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

7.1.9 Metering System

The metering system shall consist of a vacuum gauge, a leak-free pump, thermometers capable of measuring temperature to within 3°C (~5°F), a dry gas meter with 2 percent accuracy at the required sampling rate, and related equipment, or equivalent.

7.1.10 Barometer

Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 Hg (0.1 in. Hg) shall be used.

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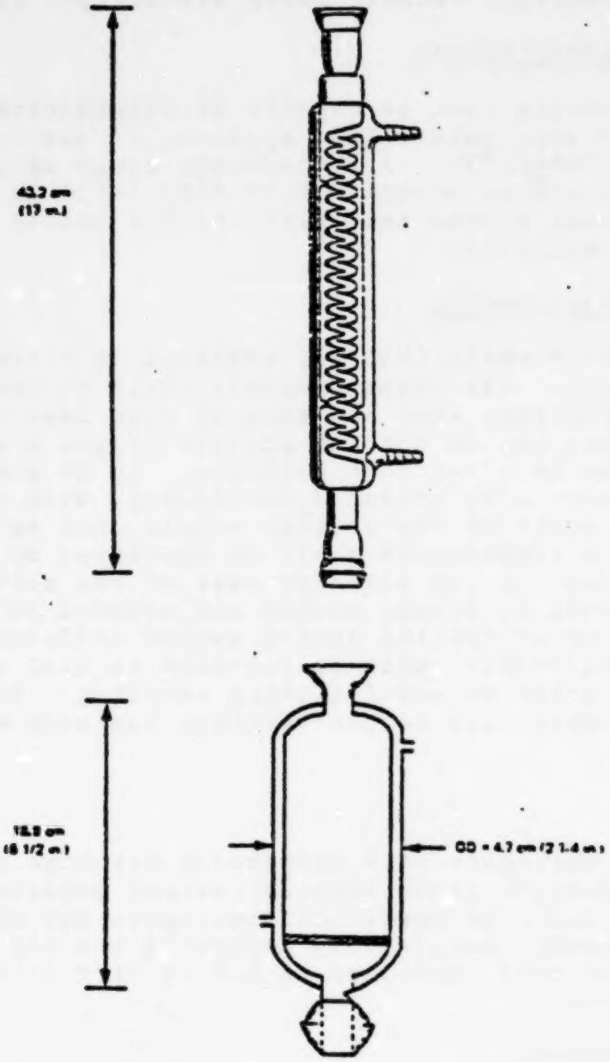
43.2 cm
(17 in.)
16.5 cm
(6 1/2 in.)
OD = 4.7 cm (2 1/4 in.)

Figure 21. Acceptable sorbent module design #1

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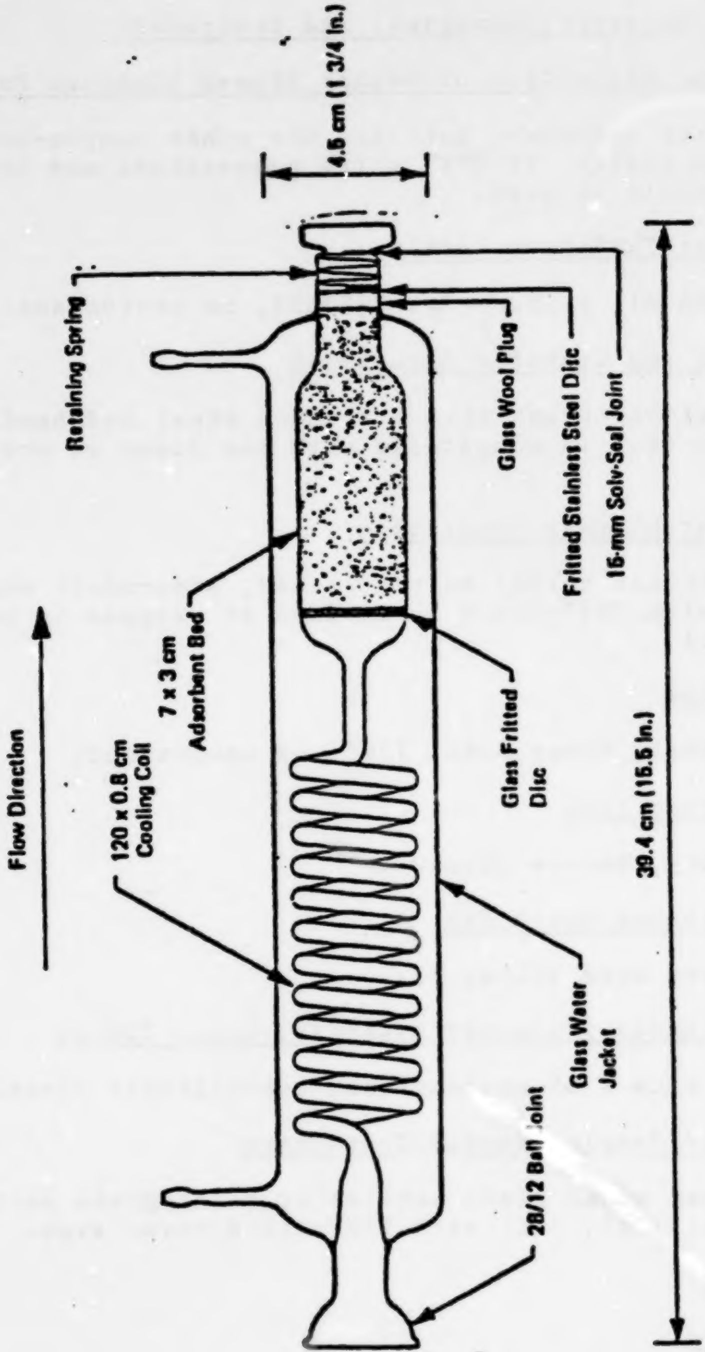
4.5 cm (1 3/4 in.)
Retaining Spring
Glass Wool Plug
Fritted Stainless Steel Disc
15-mm Solv-Seal Joint
7 x 3 cm
Adsorbent Bed
Flow Direction
120 x 0.8 cm
Cooling Coil
Glass Fritted
Disc
39.4 cm (15.5 in.)
Glass Water
Jacket
28/12 Ball Joint

Figure 3 Acceptable sorbent module design #2

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7.2 Sample Recovery, Supplies, and Equipment

7.2.1 Ground Glass Caps or Hexane Rinsed Aluminum Foil

To cap off adsorbent tube and the other sample-exposed portions of the train. If TFE® screw connections are used, then TFE® screw caps shall be used.

7.2.2 Teflon FEP® Wash Bottle

Three 500 ml, Nalgene No. 0023A59, or equivalent.

7.2.3 Probe and Transfer Line Brush

Inert bristle brush with stainless steel rod-handle of sufficient length that is compatible with the liner or probe and transfer line.

7.2.4 Filter Storage Containers

Sealed filter holder or precleaned, wide-mouth amber glass containers with TFE®-lined screw caps or wrapped in hexane rinsed aluminum foil.

7.2.5 Balance

Triple beam, Ohaus model 7505, or equivalent.

7.2.6 Aluminum Foil

Heavy duty, hexane-rinsed.

7.2.7 Precleaned Metal Can

To recover used silica gel.

7.2.8 Precleaned Graduated Cylinder, e.g., 250 ml

250 ml, with 2 ml graduations, borosilicate glass.

7.2.9 Liquid Sample Storage Containers

Precleaned amber glass bottles or clear glass bottles wrapped in opaque material, 1 L, with TFE®-lined screw caps.

8. REAGENTS

8.1 Sampling

8.1.1 Filter -- Fiberglass Reeve-Angel 934 AH or Equivalent

Prior to use in the field, each lot of filters shall be subjected to precleaning and a quality control (QC) contamination check to confirm that there are no contaminants present that will interfere with the analysis of analyte at the target detection limits.

If performed, filter precleaning shall consist of Soxhlet extraction, in batches not to exceed 50 filters, with the solvent(s) to be applied to the field samples. As a QC check, the extracting solvent(s) shall be subjected to the same concentration, cleanup and analysis procedures to be used for the field samples. The background or blank value observed shall be converted to a per filter basis and shall be corrected for any differences in concentration factor between the QC check (CF_{QC}) and the actual sample analysis procedure (CF_s).

$$\text{Blank value per filter} = \frac{\text{Apparent } \mu\text{g of analyte}}{\text{No. filters extracted}} \times \frac{CF_s}{CF_{QC}}$$

where:

$$CF = \frac{\text{Initial volume of extracting solvent}}{\text{Final Volume of concentrated extract}}$$

The quantitative criterion for acceptable filter quality will depend on the detection limit criteria established for the field sampling and analysis program. Filters that give a background or blank signal per filter greater than or equal to the target detection limit for the analyte(s) of concern shall be rejected for field use. Note that acceptance criteria for filter cleanliness depends not only on the inherent detection limit of the analysis method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

If the filters do not pass the QC check, they shall be re-extracted and the solvent extracts re-analyzed until an acceptably low background level is achieved.

8.1.2 Amberlite XAD-2 Resin

The cleanup procedure may be carried out in a giant Soxhlet extractor, which will contain enough Amberlite XAD-2® resin (XAD-2) for several sampling traps. An all glass thimble 55-90 mm OD x 150 mm deep (top to frit) containing an extra coarse frit is used ~~for~~ extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The XAD-2 must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen since it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse with 1 L H_2O for 1 cycle, then discard H_2O

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Water	Extract with H_2O for 8 hr
Methyl alcohol	Extract for 22 hr
Methylene chloride	Extract for 22 hr
Hexane	Extract for 22 hr

The XAD-2 must be dried by one of the following techniques.

(a) After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proven to be the fastest and most reliable drying method.

A simple column with suitable retainers as shown in Fig. 4 will serve as a satisfactory column. A 10.2 cm (4 in.) diameter Pyrex pipe 0.6 m (2 ft. long) will hold all of the XAD-2 from the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum XAD-2 load at the exit of the column.

The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a regular commercial liquid nitrogen cylinder has routinely proven to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95 cm (3/8 in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2 may be dried overnight consuming a full 160 L cylinder of liquid nitrogen.

As a second choice, high purity tank nitrogen may be used to dry the XAD-2. The high purity nitrogen must first be passed through a bed of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidation may cause the particles to break up.

(b) As an alternate, if the nitrogen process is not available, the XAD-2 may be dried in a vacuum oven, if the temperature never exceeds 20°C.

The XAD-2, even if purchased clean, must be checked for both methylene chloride and hexane residues, plus normal blanks before use.

(c) Storage of Clean XAD-2: XAD-2 cleaned and dried as prescribed above is suitable for immediate use in the field, provided it passes the QC contamination check described in (d), below. However, precleaned dry XAD-2 may develop unacceptable levels of

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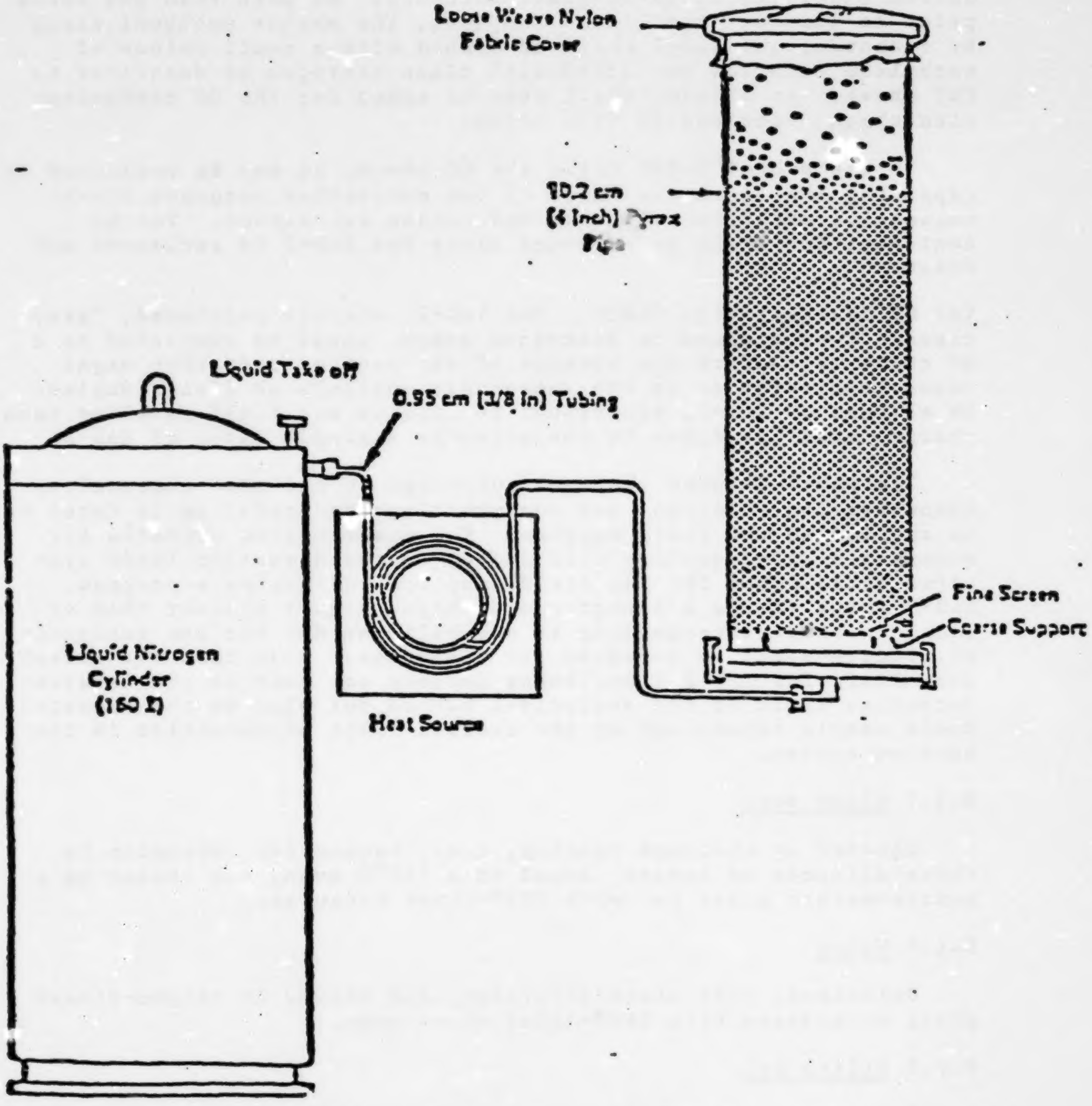
Loose Weave Nylon Fabric Cover
10.2 cm (4 inch) Pyrex Pipe
Liquid Take off
0.95 cm (3/8 in) Tubing
Fine Screen
Coarse Support
Liquid Nitrogen Cylinder (160 l)
Heat Source

Fig. 4 XAD-2 Fluidized-Bed Drying Apparatus

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contamination if stored for periods exceeding a few weeks.

If precleaned XAD-2 is not to be used immediately, it shall be stored under distilled-in-glass methanol. No more than two weeks prior to initiation of field sampling, the excess methanol shall be decanted; the XAD-2 shall be washed with a small volume of methylene chloride and dried with clean nitrogen as described in (b) above. An aliquot shall then be taken for the QC contamination check described in (d), below.

If the stored XAD-2 fails the QC check, it may be recleaned by repeating the final two steps of the extraction sequence above: sequential methylene chloride and hexane extraction. The QC contamination shall be repeated after the XAD-2 is recleaned and dried.

(d) QC Contamination Check: The XAD-2, whether purchased, "precleaned", or cleaned as described above, shall be subjected to a QC check to confirm the absence of any contaminants that might cause interferences in the subsequent analysis of field samples. An aliquot of XAD-2, equivalent in size to one field sampling tube charge, shall be taken to characterize a single batch of XAD-2.

The XAD-2 aliquot shall be subjected to the same extraction, concentration, cleanup, and analytical procedure(s) as is (are) to be applied to the field samples. The quantitative criteria for acceptable XAD-2 quality will depend on the detection limit criteria established for the field sampling and analysis program. XAD-2 which yields a background or blank signal greater than or equal to that corresponding to one-half the MDL for the analyte(s) of concern shall be rejected for field use. Note that the acceptance limit for XAD-2 cleanliness depends not only on the inherent detection limit of the analytical method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

8.1.3 Glass Wool

Cleaned by thorough rinsing, i.e., sequential immersion in three aliquots of hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

8.1.4 Water

Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with TFE®-lined screw caps.

8.1.5 Silica Gel

Indicating type, 6-16 mesh. If previously used, dry at 175±5C for 2 hr. New silica gel may be used as received.

8.1.6 Crushed Ice

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Place crushed ice in the water bath around the impingers during sampling.

9. SAMPLE RECOVERY REAGENTS

9.1 Acetone

Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

9.2 Hexane

Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

10. PROCEDURE

Caution: Sections 10.1.1.2 and 10.1.1.3 shall be done in the laboratory.

10.1 Sampling

10.1.1 Pretest Preparation

All train components shall be maintained and calibrated according to the procedure described in APTD-0576 unless otherwise specified herein.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a precleaned glass container or wrapped hexane-rinsed aluminum foil.

10.1.1.1 Preliminary Determinations

Select the sampling site and the minimum number of sampling points according to EPA Method 1. Determine the stack pressure, temperature, and the range of velocity heads using EPA Method 2; it is recommended that a leak-check of the pitot lines (see EPA Method 2, Sec. 3.1) be performed. Determine the moisture content using EPA Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate-settings. Determine the stack gas dry molecular weight, as described in EPA Method 2, Sec. 3.6; if integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the EPA Method 4 sampling.

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Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2).

Select a suitable probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min., and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume determined in Section 6.3. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid time-keeping errors.

10.1.1.2 Cleaning Glassware

All glass parts of the train upstream of and including the sorbent module and the first impinger(s) should be cleaned as described in Section 3A of the 1980 issue of "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples."[3] Special care should be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. These grease residues should be removed by soaking several hours in a chromic acid cleaning solution prior to routine cleaning as described above.

10.1.1.3 Amberlite XAD-2 Resin Trap

Use a sufficient amount (at least 30 gms or 5 gms/m^3 of stack gas to be sampled) of cleaned XAD-2 to fill completely the glass sorbent trap which has been thoroughly cleaned as prescribed and rinsed with hexane. Follow the XAD-2 with hexane-rinsed glass wool and cap both ends. These caps should not be removed until the trap is fitted into the train. See Fig. ② for details. — 1

The dimensions and XAD-2 capacity of the sorbent trap, and the volume of gas to be sampled, should be varied as necessary to ensure efficient collection of the species of interest. Some illustrative data are presented in Table 1.

10.1.2 Preparation of Collection Train

During preparation and assembly of the sampling train, keep all train openings where contamination can enter covered until

TABLE 1

SAMPLE SIZE AND FLOW RATE COMPARISON FOR SEVERAL SORBENT TRAP DESIGNS

Trap	Dimensions (mm)		Charge of XAD-2 Resin (g)	Flow Equivalent to 43 cm/sec [a]	Max. Sample Size (cm^3) ? for Efficient Capture of Following Compounds[b]		
	Depth	Diameter			Octane	Benzene	Phenol
SASS	70	90	130	165 Lpm (5.9 cfm)	150	3.0	240
ADL	70	45	40	40 Lpm (1.5 cfm)	45	0.9	74
Battelle	70	30	19	18 Lpm (0.65 cfm)	22	0.4	35

[a] Upper limit beyond which collection efficiency drops off.

[b] Calculated from Vg^T for 50% breakthrough. Specified value includes a safety factor of 2.

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just prior to assembly or until sampling is about to begin. Caution: Do not use sealant greases in assembling the train.

Place approximately 100 gms of water in each of the first two impingers with a graduated cylinder, and leave the third impinger empty. Place approximately 200 to 300 g or more, if necessary, of silica gel in the last impinger. Weigh each impinger (stem included) and record the weights on the impingers and on the data sheet.

Assemble the train as shown in Fig. 1.

Place crushed ice in the water bath around the impingers.

10.1.3 Leak Check Procedures

10.1.3.1 Initial Leak Check

The train, including the probe, will be leak checked prior to being inserted into the stack after the sampling train has been assembled. Turn on and set (if applicable) the heating/cooling system(s) to cool the sample gas yet remain at a temperature sufficient to avoid condensation in the probe and connecting line to the first impinger (approximately 120°C). Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the nozzle with a TFE® plug and pulling a 380 mm Hg (12 in. Hg) vacuum. A leakage rate in excees of 4% of the average sampling rate or 0.0057 m^3/min (0.02 cfm) whichever is less, is unacceptable. Sampling must cease if pressure during sampling exceeds the leak check pressure.

The following leak check instruction for the sampling train described in APTD-0576 (2) and APTD-0581 (4) may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until 380 mm Hg (12 in. Hg) vacuum is reached. Do not reverse the direction of the bypass valve. This will cause water to back up into the probe. If 380 mm Hg (12 in. Hg) is exceeded during the test, either leak check at this higher vacuum or end the leak check as described below and start the test over.

When the leak check is completed, first slowly remove the TFE® plug from the inlet to the probe then immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the probe.

10.1.3.2 Leak Checks During a Test

A leak check shall be performed before and after a change of port during a test. A leak check shall be performed before and after a component (e.g., filter or optional water knockout trap) is changed during a test.

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Such leak checks shall be performed according to the procedure given in Section 10.1.3.1 of this method except that it shall be performed at a vacuum equal to or greater than the highest value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is smaller) the results are acceptable. If, however, a higher leakage rate is observed, the tester shall either: (1) record the leakage rate and then correct the volume of gas sampled since the last leak check as shown in Section 10.1.3.4 of this method, or (2) void the test.

10.1.3.3 Post-Test Leak Check

A leak check is mandatory at the end of a test. This leak check shall be performed in accordance with the procedure given in Section 10.1.3.1 except that it shall be conducted at a vacuum equal to or greater than the highest value recorded during the test. If the leakage rate if found to be no greater than 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is smaller), the results are acceptable. If, however, a higher leakage rate is observed, the tester shall either: (1) record the leakage rate and correct the volume as gas sampled since the last leak check as shown in Section 10.1.3.4 of this method, or (2) void the test. 15

10.1.3.4 Correcting for Excessive Leakage Rates

The equation given in Section 11.3 of this method for calculating V_m(std), the corrected volume of gas sampled, can be used as written unless the leakage rate observed during any leak check after the start of a test exceeded L_a, the maximum acceptable leakage rate (see definitions below). If an observed leakage rate exceeds L_a, then replace V_m in the equation in Section 11.3 with the following expression:

$$[V_m - \Sigma_{i=1}^{n} (L_i-L_a)\theta_i - L_p-L_a)\theta_p]$$

where:

V_m = Volume of gas sampled as measured by the dry gas meter (dscf).

L_a = Maximum acceptable leakage rate equal to 0.00057 m^3/min. (0.02 ft^3/min) or 4% of the average sampling rate, whichever is smaller.

L_p = Leakage rate observed during the post-test leak check, m^3/min (ft^3/min).

L_i = Leakage rate observed during the leak check performed prior to the "i th" leak check (i = 1,2,3...n), m^3/min (ft^3/min).

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θ_i = Sampling time interval between two successive leak checks beginning with the interval between the first and second leak checks, min.

θ_p = Sampling time interval between the last (n th) leak check and the end of the test, min.

Substitute only for those leakages (L_i or L_p) which exceeded L_a.

10.1.3.5 Train Operation

During the sampling run, a sampling rate within 10% of the selected sampling rate shall be maintained. Data will be considered acceptable if readings are recorded at least every 5 min. and not more than 10% of the point readings are an excess of ±10% in and the average of the point readings is within ±10%. During the run, if it becomes necessary to change any system component in any part of the train, a leak check must be performed prior to restarting.

For each run, record the data required on the data sheets. An example is shown in Fig. 4. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment and when sampling is halted.

To begin sampling, remove the nozzle cap, verify (if applicable) that the probe and sorbent module temperature control systems are working and at temperature and that the probe is properly positioned. Position the probe at the sampling point. Immediately start the pump and adjust the flow rate.

If the stack is under significant sub-ambient pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to avoid water backing into the probe. If necessary, the pump may be turned on with the coarse adjust valve closed.

During the test run, make periodic adjustments to keep the probe temperature at the proper value. Add more ice and, if necessary, salt to the ice bath. Also, periodically check the level and zero of the manometer and maintain the temperature of sorbent module at or less than 20°C but above 0°C.

If the pressure drop across the train becomes high enough to make the sampling rate difficult to maintain, the test run shall be terminated unless the replacing of the filter corrects the problem. If the filter is replaced, a leak check shall be performed.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform the post test leak check.*

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*With acceptability of the test run to be based on the same criterion as in 10.1.3.1.

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FIELD DATA

PLANT ____________________
DATE ____________________
SAMPLING LOCATION ____________________
SAMPLE TYPE ____________________
RUN NUMBER ____________________
OPERATOR ____________________
BAROMETRIC PRESSURE ____________________
SITE TO BARO ELEVATION (ft) ____________________
CORRECTED B.P. ____________________
STATIC PRESSURE (P_s) ____________________
FILTER NUMBER(s) ____________________

PROBE LENGTH AND TYPE ____________________
NOZZLE I.D. ____________________
ASSUMED MOISTURE, % ____________________
SAMPLE BOX NUMBER ____________________
METER BOX NUMBER ____________________
TEMPERATURE METER NO ____________________
THERMOCOUPLE I.D. NO ____________________
METER ΔH@ ____________________
METER CORRECTION ____________________
C FACTOR ____________________
REFERENCE Δp ____________________
UMBILICAL CORD I.D. NO ____________________

LEAK CK: Initial at ≤15" Hg, CFM ____________________
Final at ______ " Hg, CFM ____________________
Pitot at ≥3" H₂O ____________________

SCHEMATIC OF TRAVERSE POINT LAYOUT
Read and Record All Data
Every ________ Minutes

$$Vm_1 = \_\_\_\_\_\_(Tm + 460)\sqrt{\frac{\Delta P_s}{Ts + 460}}$$

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft³		VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
		Desired	Actual		DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F		XAD-2	

COMMENTS

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10.2 Sample Recovery

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safety handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with hexane-rinsed aluminum foil. Seal off the inlet to the train with a ground glass cap or hexane-rinsed aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area should be clean and enclosed so that the chances of contaminating or losing the sample will be minimized. No smoking shall be allowed.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broker filters, color of the impinger liquid, etc. Treat the samples as follows:

10.2.1 Container No. 1

Either seal the ends of the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of precleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and/or a sharp-edged blade. Seal the container.

10.2.2 Sorbent Modules

Remove the sorbent module from the train and cap it off.

10.2.3 Cyclone Catch

If the optional cyclone is used, quantitatively recover the particulate into a sample container and cap.

10.2.4 Sample Container No. 2

Quantitatively recover material deposited in the nozzle, probe, transfer line, the front half of the filter holder, and the cyclone, if used, first by brushing and then by sequentially rinsing with acetone and then hexane three times each and add all these rinses to Container No. 2. Mark level of liquid on container.

10.2.5 Sample Container No. 3

Rinse the back half of the filter holder, the connecting line between the filter and the condenser and the condenser (if using the separate condenser-sorbent trap) three times each with acetone and hexane collecting all rinses in Container 3. If using the combined condenser-sorbent trap, the rinse of the condenser shall be performed in the laboratory after removal of the XAD-2. If the optional water knockout trap has been employed, it shall be weighed and recorded and its contents placed in Container 3 along with the rinses of it. Rinse it three times each with acetone, and hexane. Mark level of liquid on container.

10.2.6 Sample Container No. 4

Remove the first impinger. Wipe off the outside of the impinger to remove excessive water and other material, weigh (stem included), and record the weight on data sheet. Pour the contents and rinses directly into Container No. 4. Rinse the impinger sequentially three times with acetone, and hexane. Mark level of liquid on container.

10.2.7 Sample Container No. 5

Remove the second and third impingers, wipe the outside to remove excessive water and other debris, weigh (stem included) and record weight on data sheet. Empty the contents and rinses into Container No. 5. Rinse each with distilled DI water three times. Mark level of liquid on container.

10.2.8 Silica Gel Container

Remove the last impinger, wipe the outside to remove excessive water and other debris, weigh (stem included), and record weight on data sheet. Place the silica gel into its marked container.

11. CALCULATIONS

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

11.1 Nomenclature

G_s = Total weight of chlorinated organic compounds in stack gas sample, ng.

C_s = Concentration of chlorinated organic compounds in stack gas, $\mu g/m^3$, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

I = Percent of isokinetic sampling.

M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-$m^3/^oK$-g-mole (21.83 in. Hg-$ft^3/^oR$-lb-mole).

T_m = Absolute average dry gas meter temperature ^oK (^oR).

T_s = Absolute average stack gas temperature ^oK (^oR).

T_{std} = Standard absolute temperature, 293^oK (68^oF).

m_{lc} = Total mass of liquid collected in impingers and silica gel.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_m(std)$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

$V_w(std)$ = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf).

v_s = Stack gas velocity, calculated by combustion calculation, m/sec (ft/sec).

Y = Meter box correction factor.

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml).

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

11.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop

See data sheet (Fig. 4).

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11.3 Dry Gas Volume

Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68±F, 29.92 in. HG)] by using Equation 1.

$$V_m(std) = Y\ V_m \frac{T_{std} + d}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} = K_1 V_m \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m} \qquad (1)$$

where:

K_1 = 0.3855 °K/mm Hg for metric units

= 17.65 °R/in. Hg for English units

11.4 Volume of Water Vapor

$$V_w(std) = m_{1c} \frac{RT_{std}}{M_w \times P_{std}} = K_2 m_{1c} \qquad (2)$$

where:

K_2 = 0.00134 m^3/ml for metric units

= 0.0472 ft^3/ml for English units

11.5 Moisture Content

$$B_{ws} = \frac{V_{w(std)}}{V_m(std) + V_{w(std)}} \qquad (3)$$

If liquid droplets are present in the gas stream assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

11.6 Percent Isokinetic Sampling

$$I = \frac{100\ T_s\ [K_4\ Mlc + (Vm\ Km)\ (P_{bar} + \Delta H/13.6)]}{60\ \theta_{vs}\ P_s\ A_n} \qquad (4)$$

where:

K_4 = 0.003454 mm Hg - m^3/ml - °K for metric units

= 0.002669 in Hg - ft^3/ml - °R for English units

11.7 Concentration of Chlorinated Organic Compounds in Stack Gas

Determine the concentration of chlorinated organic compounds in the stack gas according to Equation 5.

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$$C_s = K_5 \frac{G_s}{V_m(std)} \qquad (5)$$

where:

$$K_5 = 35.31\ ft^3/m^3$$

12. QUALITY ASSURANCE (QA) PROCEDURES

The positive identification and quantification of specific compounds in this assessment of stationary conventional combustion sources is highly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in this section were designed to monitor the performance of the sampling methods and to provide information to take corrective actions if problems are observed.

Field Blanks

The field blanks should be submitted as part of the samples collected at each particular testing site. These blanks should consist of materials that are used for sample collection and storage and are expected to be handled with exactly the same procedure as each sample medium.

Blank Train

For each series of test runs, set up a blank train in a manner identical to that described above, but with the probe inlet capped with hexane-rinsed aluminum foil and the exit end of the last impinger capped with a ground glass cap. Allow the train to remain assembled for a period equivalent to one test run. Recover the blank sample as described in Sec. 7.2.

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APPENDIX B

DRAFT ASME ANALYTICAL PROTOCOL

"ANALYTICAL PROCEDURES TO ASSAY STACK EFFLUENT SAMPLES AND RESIDUAL COMBUSTION PRODUCTS FOR POLYCHLORINATED DIBENZO-P-DIOXINS (PCDD) AND POLYCHLORINATED DIBENZOFURANS (PCDF)

DRAFT, SEPTEMBER 18, 1984

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ANALYTICAL PROCEDURES TO ASSAY STACK EFFLUENT SAMPLES AND RESIDUAL COMBUSTION PRODUCTS FOR POLYCHLORINATED DIBENZO-p-DIOXINS (PCDD) AND POLYCHLORINATED DIBENZOFURANS (PCDF)

Prepared By

GROUP C - ENVIRONMENTAL STANDARDS WORKSHOP

Sponsored By

THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS, U.S. DEPARTMENT
OF ENERGY AND U.S. ENVIRONMENTAL PROTECTION AGENCY

SEPT. 18, 1984

1. Scope and Applicability of Method

The analytical procedures described here are applicable for the determination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in stack effluents from combustion processes. These methods are also applicable to residual combustion products such as bottom and precipitator ash. The methods presented entail addition of isotopically-labeled internal standards to all samples in known quantities, extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of the extracts using a sequence of liquid chromatography columns, and analysis of the processed extract for PCDD and PCDF using coupled gas chromatography - mass spectrometry (GC-MS). Various performance criteria are specified herein which the analytical data must satisfy for quality assurance purposes. These represent minimum criteria which must be incorporated into any program in which PCDD and PCDF are determined in combustion product samples.

The method presented here does not yield definitive information on the concentration of individual PCDD/PCDF isomers, except for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8-Tetrachlorodibenzofuran (TCDF). Rather, it is designed to indicate the total concentration of the isomers of several chlorinated classes of PCDD/PCDF (that is, total tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins and dibenzofurans). Of the 75 separate PCDD and 135 PCDF isomers, there are 22 TCDD, 38 TCDF, 14 PeCDD, 28 PeCDF, 10 HxCDD, 16 HxCDF, 2 HpCDD, 4 HpCDF, 1 OCDD and 1 OCDF.[a]

The analytical method presented herein is intended to be applicable for determining PCDD/PCDF present in combustion products at the ppt to ppm level, but the sensitivity which can ultimately be achieved for a given sample will depend upon the types and concentrations of other chemical compounds in the sample.

The method described here must be implemented by or under the supervision of chemists with experience in handling supertoxic materials and analyses should only be performed in rigorously controlled, limited access laboratories. The quantitation of PCDD/PCDF should be accomplished only by analysts experienced in utilizing capillary-column gas chromatography-mass spectrometry to accomplish quantitation of chlorocarbons and similar compounds at very low concentration.

The toxicological data which are available for the PCDD and PCDF are far from complete. That is, the toxicological properties of all of the isomers comprising the 75 possible PCDD and 135 possible PCDF are not presently known. However, a considerable body of toxicological data exists for 2,3,7,8-TCDD which indicates that, in certain animal species, this compound is lethal at extraordinarily low does and causes a wide range of systemic affects, including hepatic disorders, carcinoma and birth defects. While much less data is available regarding the toxicology of 2,3,7,8-TCDF, sufficient data is available to form the basis for the belief that 2,3,7,8-TCDF is similar in its toxicological properties to 2,3,7,8-TCDD. Relatively little is known about the toxicology of the higher chlorinated PCDD and PCDF (that is, penta through octachlorinated PCDD/PCDF), although there is some data to suggest that certain penta-, hexa-, and hepta- PCDD/PCDF isomers are hazardous. In view of the extraordinary toxicity of 2,3,7,8-TCDD and in view of the exceptional biological activity of this compound (on the basis of enzyme induction assays) and of compounds having similar molecular structures, extensive precautions are required to preclude exposure to personnel during handling and analysis of materials containing these compounds and to prevent contamination of the laboratory. Specific safety and handling procedures which are recommended are given in the Appendix to this protocol.

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a. The abbreviations which are used to designate chlorinated dibenzo-p-dioxins and dibenzofurans throughout this document are as follows:

PCDD - Any or all of the 75 possible chlorinated dibenzo-p-dioxin isomers

PCDF - Any or all of the 135 possible chlorinated dibenzofuran isomers

TCDD - Any or all of the 22 possible tetrachlorinated dibenzo-p-dioxin isomers

TCDF - Any or all of the 138 possible tetrachlorinated dibenzofuran isomers

PeCDD - Any or all of the 14 possible pentachlorinated dibenzo-p-dioxin isomers

PeCDF - Any or all of the 28 possible pentachlorinated dibenzofuran isomers

HxCDD - Any or all of the 10 possible hexachlorinated dibenzo-p-dioxin isomers

HXCDF - Any or all of the 16 possible hexachlorinated dibensofuran isomers

HpCDD - Any or all of the 2 possible heptachlorinated dibenzo-p-dioxin isomers

HpCDF - Any or all of the 4 possible heptachlorinated dibenzofuran isomers

OCDD - Octachlorodibenzo-p-dioxin

OCDF - Octachlorodibenzofuran

Specific Isomers. - Any of the abbreviations cited above may be converted to designate a specific isomer by indicating the exact positions (carbon atoms) where chlorines are located within the molecule. For example, 2,3,7,8-TCDD refers to only one of the 22 possible TCDD isomers - that isomer which is chlorinated in the 2,3,7,8 po[illegible]ns of the dibenzo-p-dioxin ring structure.

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2. Reagents and Chemicals

The following reagents and chemicals are appropriate for use in these procedures. In all cases, equivalent materials from other suppliers may also be used.

2.1 Potassium Hydroxide, Anhydrous, Granular Sodium Sulfate and Sulfuric Acid (all Reagent Grade): J. T. Baker Chemical Co. or Fisher Scientific Co. The granular sodium sulfate is purified prior to use by placing a beaker containing the sodium sulfate in a 400°C oven for four hours, then removing the beaker and allowing it to cool in a desiccator. Store the purified sodium sulfate in a bottle equipped with a Teflon-lined screw cap.

2.2 Hexane, Methylene Chloride, Benzene, Methanol, Toluene, Isooctane: "Distilled in Glass" Burdick and Jackson.

2.3 Tridecane (Reagent Grade): Sigma Chemical Co.

2.4 Basic Alumina (Activity Grade 1, 100 - 200 mesh): ICN Pharmaceuticals. Immediately prior to use, the alumina is activated by heating for at least 16 hours at 600°C in a muffle furnace and then allowed to cool in a desiccator for at least 30 minutes prior to use. Store pre-conditioned alumina in a desiccator.

2.5 Silica (Bio-Sil A,100/200 mesh): Bio-Rad. The following procedure is recommended for conditioning the Bio-Sil A prior to use. Place an appropriate quantity of Bio-Sil A in a 30 mm x 300 mm long glass tube (the silica gel is held in place by glass wool plugs) which is placed in a tube furnace. The glass tube is connected to a pre-purified nitrogen cylinder, through a series of four traps (stainless steel tubes, 1.0 cm O.D. x 10 cm long)[6]: 1) Trap No. 1 - Mixture comprised of Chromosorb W/AW (60/80 mesh coated with 5% Apiezon L), Graphite (UCP-1-100), Activated Carbon (50 to 200 mesh) in a 7:1.5:1.5 ratio (Chromosorb W/AW, Apiezon L obtained from Supelco, Inc., Graphite obtained from Ultracarbon Corporation, 100 mesh, 1-M-USP; Activated Carbon obtained from Fisher Scientific Co.); 2) Trap No. 2 - Molecular Sieve 13 X (60/80 mesh), Supelco, Inc.; 3) Trap No. 3 - Carbosieve S (80/100 mesh), obtained from Supelco, Inc.; 4) The Bio-Sil A is heated in the tube for 30 minutes at 180°C while purging with nitrogen (flow rate 50-100 mL/minute), and the tube is then removed from the furnace and allowed to cool to room temperature. Methanol (175 mL) is then passed through the tube, followed by 175 mL methylene chloride. The tube containing the silica is then returned to the furnace, the nitrogen purge is again established (50-100 mL flow) and the tube is heated at 50°C for 10 minutes, then the temperature is gradually increased to 180°C over 25 minutes and maintained at 180°C for 90 minutes. Heating is then discontinued but the nitrogen purge is continued until the tube

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cools to room temperature. Finally, the silica is transferred to a clean, dry, glass bottle and capped with a Teflon-lined screw cap for storage.

2.6 Silica Gel Impregnated With Sulfuric Acid: Concentrated sulfuric acid (44 g) is combined with 100 g Bio-Sil A (conditioned as described above) in a screw capped bottle and agitated to mix thoroughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The H_2SO_4-silica gel is stored in a screw-capped bottle (Teflon-lined cap).

2.7 Silica Gel Impregnated with Sodium Hydroxide: 1N Sodium hydroxide (39 g) is combined with 100 g Bio-Sil A (conditioned as described above) in a screw capped bottle and agitated to mix throughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The NaOH-silica gel is stored in a screw-capped bottle (Teflon-lined cap).

2.8 Carbon/Celite:
Carbon: Amoco PX-21
Celite 545: Fisher Scientific Co

Combine Amoco PX-21 carbon (10.7 g) with Celite 545 (124 g) in a 250 mL glass bottle fitted with a Teflon-lined cap. Agitate the mixture to combine thoroughly. Store in the screw-capped bottle.

2.9 Sepralyte Diol (40μ): Analytichem International

2.10 Nitrogen and Hydrogen (Ultra High Purity): Matheson Scientific

3. Apparatus and Materials

The following apparatus and materials are appropriate for use in these procedures. In all cases, equivalent items from other suppliers may also be used.

3.1 Glassware used in the analytical procedures (including the Soxhlet apparatus and disposable bottles) is cleaned by rinsing successively three times with methanol and then three times with methylene chloride, and finally drying it in a 100°C oven. Bottles cleaned in this manner are allowed to cool to room temperature and are then capped using Teflon-lined lids. Teflon cap liners are rinsed as just described but are allowed to air-dry. More rigorous cleaning of some glassware with detergent may be required prior to the solvent rinses, for example, the glassware employed for Soxhlet extraction of samples.

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3.1.1 Sample Vessels: 125 mL and 250 mL flint glass bottles fitted with screw caps and teflon cap liners, and glass test tubes, VWR-Scientific.

3.1.2 Teflon Cap Liners: Scientific Specialities Service, Inc.

3.1.3 Soxhlet Apparatus: Extraction apparatus, Allihn condenser, Kimax Brand, American Scientific Products Cat. No. E6252-2A.

3.1.4 Gravity Flow Liquid Chromatographic Columns: Custom Fabricated (Details of the columns are provided in later sections).

3.1.5 Micro-vials (3.0 mL): Reliance Glass.

3.2 Capillary Gas Chromatographic Columns: Two different columns are required if data on both 2,3,7,8-TCDD and 2,3,7,8-TCDF, as well as on the total PCDD/PCDF by chlorinated class, are desired. The appropriate columns are: 1) A fused silica column (60 M x 0.25 mm I.D.) coated with DB-5 (0.25 µ film thickness), J & S Scientific, Inc., Crystal Lake, IL is utilized to separate each of the several tetra-through octachlorinated CDDs and CDFs, as a group, from all of the other groups. While this column does not resolve all of the isomers within each chlorinated group, it effectively resolves each of the chlorinated groups from all of the other chlorinated groups and therefore provides data on the total concentration of each group (that is, total tetra-, penta-, hexa-, hepta- and octa CDDs and CDFs). This column also resolves 2,3,7,8-TCDD from all of the other 21 TCDD isomers and this isomer can therefore be determined quantitatively if proper calibration procedures are applied as described further in a later section. This column does not completely resolve 2,3,7,8-TCDF from the other TCDF isomers, and if a peak corresponding in retention time to 2,3,7,8-TCDF is observed in the analysis using this column, then a portion of the sample extract must be reanalyzed using the second GC column described below if isomer - specific data on 2,3,7,8-TCDF is desired. 2) A fused silica column (30 M x 0.25 mm I.D.) coated with DB-225 (0.25 µ film thickness), J & S Scientific, Inc., Crystal Lake, IL, must be utilized to obtain quantitative data on the concentration of 2,3,7,8-TCDF, since this column adequately resolves 2,3,7,8-TCDF from the other TCDF isomers.

3.3 Balance: Analytical Balance, readibility, 0.0001 g.

3.4 Nitrogen Blowdown Concentration Apparatus: N-Evap Analytical Evaporator Model III, Organomation Associates Inc.

3.5 Tube Furnace: Lindberg Type 59344.

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4. Instrumentation

Gas Chromatograph-Mass Spectrometer-Data System (GC/MS/DS): The instrument system used to analyze sample extracts for PCDD/PCDF comprises a gas chromatograph (fitted for capillary columns) coupled directly or through an enrichment device to a mass spectrometer which is equipped with a computer-based data system. The individual components of the GC/MS/DS are described below.

4.1 Gas Chromatograph (GC): The chromatograph must be equipped with an appropriate injector and pneumatic system to permit use of the specified glass or fused silica capillary columns. It must also incorporate an oven which can be heated in a reproducible, programmed temperature cycle. The injector should be configured for splitless/ split injections. The GC column performance should be verified at the beginning of each 8 hour work period or at the beginning of each series of analyses if more than one set of samples is analyzed during an 8 hour shift. Extracts of complex combustion products and effluents may contain numerous organic residues even after application of the extensive prefractionation/cleanup procedures specified in this method. These residues may result in serious deviation of GC column performance and therefore, frequent performance checks are desirable. Using appropriate calibration mixtures, as described below, the retention time windows for each chlorinated class of CDDs/CDFs must be verified. In addition, the GC column utilized must be demonstrated to effectively separate 2,3,7,8-TCDD from all other TCDD isomers if data on 2,3,7,8-TCDD alone is desired with at least 20% valley definition between the 2,3,7,8- isomer and the other adjacent-eluting TCDD isomers. Typically, capillary column peak widths (at half-maximum peak height) on the order of 5-10 seconds are obtained in the course of these analyses. An appropriate GC temperature program for the analyses described herein is discussed in a later section (see Table 1).

4.2 Gas Chromatograph-Mass Spectrometer Interface: The GC-MS interface can include enrichment devices, such as a glass jet separator or a silicone membrane separator, or the gas chromatograph can be directly coupled to the mass spectrometer source, if the system has adequate pumping of the source region. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless steel. The interface components must be compatible with temperatures in the neighborhood of 250°C, which is the temperature at which the interface is typically maintained throughout analyses for PCDD/PCDF. The GC/MS interface must be appropriately configured so that the separation of 2,3,7,8-TCDD from the other TCDD isomers which is achieved in the gas chromatographic column is not appreciably degraded. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. If the latter are observed, thorough cleaning of the injection port, interface and connecting lines should be accomplished prior to proceeding.

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4.3 Mass Spectrometer (MS): The mass spectrometer used for the analyses described here is typically a double-focusing sector or quadrupole instrument equipped with an electron impact source (70 ev), maintained at 250°C, and a standard electron multiplier detector. If possible, it is desirable to have both low and high resolution capability with the mass spectrometer used, since confirmation of data obtained by low resolution MS using high resolution MS is sometimes desirable. Alternatively, a combination of mass spectrometers can be used for this purpose. The static resolution of the instrument must be maintained at a minimum of 1:500 (with a 10% valley between adjacent masses) if operating in the low resolution MS mode, and a minimum resolution of 1:10,000 is desirable for operation in the high resolution mode. The mass spectrometer must also be configured for rapid computer-controlled selected-ion monitoring in both high and low resolution operating modes. At a minimum, two ion-masses characteristic of each class of chlorinated dioxins should be monitored, and these are two ions in the molecular ion isotopic cluster. It is desirable for increased confidence in the data to also monitor the fragment ions arising from the loss of COCl from the molecular ion. In order to accomplish the requisite rapid multiple ion monitoring sequence during the time period defined by a typically capillary chromatographic peak (the base of the chromatographic peak is typically 15-20 seconds in width), the following MS performance parameters are typically required (assuming a 4-ion monitoring sequence for each class of PCDD/PCDF): dwell time/ion-mass, ≈100 msec.; minimum number of data points/chromatographic peak, 7 . The mass scale of the mass spectrometer is calibrated using high boiling perfluorokerosene and/or some other suitable mass standard depending upon the requirements of the GC-MS-DS system utilized. The actual procedures utilized for calibration of the mass scale will be unique to the particular mass spectrometer being employed. A list of the appropriate ions to be monitored in the PCDD/PCDF analyses described herein is presented in a later section (see Table 1).

4.4 Data System: A dedicated computer-based data system, capable of providing the data described above, is employed to control the rapid selected-ion monitoring sequence and to acquire the data. Both digital data (peak areas or peak heights) as well as peak profiles (displays of intensities of ion-masses monitored as a function of time) should be acquired during the analyses, and displayed by the data system. This raw data (mass chromatograms) should be provided in the report of the data.

5. Calibration Standards

A recommended set of calibration standards to be used in the analyses described herein is presented below. Stock standard solutions of the various PCDD and PCDF isomers and mixtures thereof are prepared in a glovebox, using weighed quantities of the authentic isomers.[b] These stock solutions are contained in appropriate volumetric flasks and are stored tightly stoppered, in a refrigerator. Aliquots of the stock standards are removed for direct use or for subsequent serial dilutions to prepare working standards. These standards must be checked regularly (by comparing instrument response factors for them over a period of time) to ensure that solvent evaporation or other losses have not occurred which would alter the standard concentration. The several recommended standard solutions are as follows.

5.1 Standard Mixture A: Prepare a stock solution containing the following isotopically-labelled PCDD and PCDF in isooctane at the indicated concentrations: 2.5ng./µl$^{13}C_{12}$-2,3,7,8-TCDD, 2.5ng/µl$^{37}Cl_4$-2,3,7,8-TCDF, 25ng/µL$^{13}C_{12}$-1,2,3,4,7,8-HxCDD, 25ng/µL$^{13}C_{12}$-1,2,3,4,7,8-HxCDF, 25ng/µL$^{13}C_{12}$-OCDD, and 25ng/µL$^{13}C_{12}$-OCDF. Portions of this isomer mixture are added to all samples prior to analyses and serve as internal standards for use in quantitation. Recovery of these standards is also used to guage the overall efficacy of the analytical procedures.

5.2 Standard B: Prepare a stock solution containing 1.0 ng of $^{37}Cl_4$-2,3,7,8-TCDD/µL of isooctane. This standard can be coinjected if desired, along with aliquots of the final sample extract to reliably estimate the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD surrogate standard.

5.3 Standard Mixture C: Prepare a stock solution containing 100 ng/µL of isooctane of each of the following PCDD and PCDF: 2,3,7,8-TCDF; 2,3,7,8-TCDD; 1,3,4,6,8-PeCDF, 2,3,4,6,7-PeCDF; 1,2,4,7.9-PeCDD; 1,2,3,8,9-PeCDD; 1,2,3,4,6,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,4,6,8-HxCDD, 1,2,3,4,6,7-HxCDD; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,9-HpCDD; OCDF: and OCDD. This isomer mixture is used to define the gas chromatographic retention time intervals or windows for each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. Each pair of isomers of a given chlorinated class which is listed here corresponds to the first and last eluting isomers of that class on the DB-5 capillary GC column (except for TCDD and TCDF). In addition, this isomer mixture is used to determine GC-MS response factors for representative isomers of each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. The later data are used in quantitating the analytes in unknown samples.

5.4 Standard Mixture D: Prepare a stock solution containing 50 pg/µL of isooctane of each of the following TCDD isomers: 1,3,6,8-TCDD; 1,2,3,7-TCDD; 1,2,3,9-TCDD; 2,3,7,8-TCDD; and 1,2,8,9-TCDD. Two of the isomers in this mixture are used to define the gas chromatographic retention time window for TCDDs (1,3,6,8-TCDD is the first eluting TCDD

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[b] Some of the PCDD/PCDF isomer standards recommended for this method are available from Cambridge Isotope Laboratories, Cambridge, Massachusetts. Other PCDD/PCDF standards are available from the Brehm Laboratory, Wright State University, Dayton, Ohio, from the U.S. EPA Standard Repository at Research Triangle Park, North Carolina and possibly from other laboratories. Not all of the indicated isotopically-labelled PCDD/PCDF internal standards recommended here are presently available in quantities sufficient for widespread distribution, but these are expected to be available in the near future.

isomer and 1,2,8,9-TCDD is the last eluting TCDD isomer on the DB-5 GC column). The remaining isomers serve to demonstrate that the 2,3,7,8-TCDD isomer is resolved from the other nearest eluting TCDD isomers, and that the column therefore yields quantitative data for the 2,3,7,8-TCDD isomer alone.

5.5 Standard Mixture E: Prepare a stock solution containing 50 pg/µL of isooctane of each of the following TCDF isomers: 1,3,6,8-TCDF; 2,3,4,8-TCDF; 2,3,7,8-TCDF, 2,3,4,7-TCDF; and 1,2,8,9-TCDF. This isomer mixture is used to define the TCDF gas chromatographic retention time window (1,3,6,8- and 1,2,8,9-TCDF are the first and last eluting TCDFs on the DB-5 capillary column) and to demonstrate that 2,3,7,8-TCDF is uniquely resolved from the adjacent-eluting TCDF isomers.

6. Procedures for Addition of Internal Standards and Extraction of Samples

Both liquid and solid samples will be obtained for PCDD/PCDF analyses as a result of the application of an appropriate stack sampling procedure. Samples resulting from the sampling train will include the following (these will be provided to the analytical laboratory as separate samples in the form indicated): 1) particulate filter and particulates thereon; 2) particulates from the cyclone (if used); 3) combined aqueous solutions from the impingers; 4) the intact XAD-resin cartridge and the resin therein; 5) combined aqueous rinse (if used) solutions from rinses of the nozzle, probe, filter holder, cyclone (if used), impingers, and all connecting lines; 6) combined acetone rinse solutions from rinses of the nozzle, probe, filter holder, cyclone (if used), impingers, and all connecting lines; 7) combined hexane rinse solutions from rinses of the nozzle, probe, filter, cyclone (if used), impingers, and all connecting lines. In addition, samples of bottom ash, precipitator ash, incinerator feed materials or fuel, quench liquids, and materials from effluent control devices may also be provided for analyses.

In general, the volumes of all liquid samples received for analyses are measured and recorded, and where appropriate, solid samples or aliquots thereof are weighed. Any samples which are homogeneous (as for example, a single liquid phase sample or a solid which can be thoroughly mixed) can be split prior to analyses, if desired, provided that this will still permit the attainment of the desired detection limits for the analytes of interest. Samples such as particulates from the sampling train which are generally collected in relatively small quantity, are preferably analyzed in total.

6.1 Organic Liquid Samples (Acetone and Hexane Solutions) Concentrate each of the combined organic liquids (acetone and hexane solutions) to a volume of about 1-5 mL using the nitrogen blowdown apparatus (a stream of dry nitrogen) while heating the sample gently on a water bath. Pool the concentrated residues, rinsing the vessels three times with small portions of hexane and adding these to the residues, and concentrate to near dryness. This residue will likely contain particulates which were removed in the rinses of the train probe and nozzle. Combine the residue (along with three rinses of the final sample vessel) in the Soxhlet apparatus with the filter and particulates, and proceed as described under Solid Sample below.

6.2 Aqueous Liquids

Add an appropriate quantity of the isotopically-labeled internal standard mixture (Standard Mixture A described earlier) to the aqueous liquid sample (or an aliquot thereof) in a screw-capped bottle fitted with a Teflon-lined cap. Add approximately 25% by volume of hexane to the spiked aqueous sample, seal the bottle and agitate on a shaker for a period of three hours. Allow the vessel to stand until the aqueous and organic layers separate, then transfer the organic layer to a separate sample bottle. Repeat the hexane extraction sequence two additional times and combine the organic fractions with that from the first extraction. Proceed with the sample fractionation and cleanup procedures described below.

6.3 Solid Samples

Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene and reflux for a period of one hour. Remove the toluene and discard it, retaining the silica gel, or if desired, retain a portion of the toluene to check for background contamination. For extraction of particulates, place the entire sample in the thimble onto the bed of precleaned silica gel (1 cm. thick), and top with the precleaned glass wool retained from the initial Soxhlet cleaning procedure. Add the appropriate quantity of the isotopically-labelled internal standard mixture (Standard Mixture A described earlier) to the sample in the Soxhlet thimble. Charge the Soxhlet with toluene and reflux for a period of 16 hours. After extraction, allow the Soxhlet to cool, remove the toluene extract, and transfer it to another sample vessel. Concentrate the extract to a volume of approximately 40 ml by using the nitrogen blowdown apparatus described earlier. Proceed with the sample fractionation and cleanup procedures described below.

7. Procedures for Cleanup and Fractionation of Sample Extracts

The following column chromatographic sample clean-up procedures are used in the order given, although not all may be required. In general, the silica and alumina column procedures are considered to be a minimum requirement. Acceptable alternative cleanup procedures may be used provided that they are demonstrated to effectively transmit a representative set of the analytes of interest. The column chromatographic procedures listed here have been demonstrated to be effective for a mixture consisting of 1,2,3,4-TCDD, 2,3,7,8-TCDD 2,3,6,8-TCDF, 1,2,4,8-TCDF, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDD, 1,2,4,6,7.9-HxCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,8,9-HpCDF, OCDD and OCDF

An extract obtained as described in the foregoing sections is concentrated to a volume of about 1 mL using the nitrogen blowdown apparatus, and this is transferred quantitatively (with rinsings) to the combination silica gel column described below.

7.1 Combination Silica Gel Column: Pack one end of a glass column (20 mm. O.D. x 230 mm in length) with glass wool (precleaned) and add, in sequence, 1 g silica gel, 2 g base-modified silica gel, 1 g silica gel, 4 g acid-modified silica gel, and 1 g silica gel. (Silica gel and modified silica gel are prepared as described in the Reagents sections of this protocol.) Preelute the column with 30 mL hexane and discard the eluate. Add the sample extract in 5 mL of hexane to the column along with two additional 5 ml rinses. Elute the column with an additional 90 mL of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml.

7.2 Basic Alumina Column: Cut off a 10 mL disposable Pasteur glass pipette at the 4 mL graduation mark and pack the lower section with glass wool (precleaned) and 3 g of Woelm basic alumina (prepared as described in the Reagent section of this protocol). Transfer the concentrated extract from the combination silica column to the top of the column and elute the column sequentially with 15 mL of hexane, 10 mL of 8% methylene chloride-in-hexane and 15 mL of 50% methylene chloride-in-hexane, discarding the first two eluate fractions and retaining the third eluate fraction. Concentrate the latter fraction to about 0.5 mL using the nitrogen blowdown apparatus described earlier.

7.3 PX-21 Carbon/Celite 545 Column: Take a 9 inch disposable Pasteur pipette and cut off a 0.5 inch section from the constricted tip. Insert a filter paper disk at the top of the tube, 2.5 cm. from the constriction. Add a sufficient quantity of PX-21 Carbon/Celite 545 (Prepared as described in the reagent section of this protocol) to the tube to form a 2 cm. length of the Carbon-Celite. Insert a glass wool plug. Preelute the column in sequence with 2 mL of 50% benzene-in-ethyl acetate, 1 mL of 50% methylene chloride-in-cyclohexane and 2 mL of hexane, and discard these eluates. Load the extract (in 1 mL of hexane) from the alumina column onto the top of the column, along with 1 mL hexane rinse. Elute the column with 2 mL of 50% methylene chloride-in-hexane and 2 mL of 50% benzene-in-ethyl acetate and discard these eluates. Invert the column and reverse elute it with 4 mL of toluene, retaining this eluate. Concentrate the eluate and transfer it to a Reacti-Vial for storage. Store extracts in a freezer, shielded from light, prior to GC-MS analysis. If desired, still another column chromatographic clean-up step can be employed prior to concentration of the extract, as described below.

7.4 Silica/Diol Micro Column Cleanup: After the above clean-up steps small amounts of highly colored polar compounds may be present in complex samples. These are removed, if necessary, by the following column: Push a small plug of glass wool into a disposable 6 mm i.d. glass Pasteur pipette, followed by 3 mm of Sepralyte (Analytichem International), 6 mm of silica gel and finally 3 mm of sodium sulfate. The column is pre-wet with hexane, the sample is applied in 100 µL of 100% hexane and eluted with hexane, collecting 1.5 ml.

8. Procedure for Analysis of Sample Extracts for PCDD/PCDF Using Gas Chromatography-Mass Spectrometry (GC-MS).

8.1 Sample extracts prepared by the procedures described in the foregoing are analyzed by GC-MS utilizing the following instrumental parameters. Typically, 1 to 5 µL portions of the extract are injected into the GC. Sample extracts are first analyzed using the DB-5 capillary GC column to obtain data on the concentrations of total tetra-through octa-CDDs and CDFs, and on 2,3,7,8-TCDD. If tetra-CDFs are detected in this analysis, then another aliquot of the sample is analyzed in a separate run, using the DB-225 column to obtain data on the concentration of 2,3,7,8-TCDF.

8.2 Gas Chromatograph

8.2.1 Injector: Configured for capillary column, splitless/split injection (split flow on 60 seconds following injection), injector temperature, 250°C.

8.2.2 Carrier gas: Hydrogen, 30 lb head pressure.

8.2.3 Capillary Column 1: For total tetra- through octa - CDDs/CDFs and 2,3,7,8-TCDD, 60 M x 0.25 mm I.D. fused silica DB-5; temperature programmed (see Table 1 for temperature program). Capillary Column 2: for 2,3,7,8-TCDF only, 60 M x 0.25 mm I.D. fused silica DB-225, temperature programmed (180°C for 1 min., then increase from 180°C to 240°C @ 5°C/min., hold at 240°C for 1 min.)

8.2.4 Interface Temperature: 250°C

8.3 Mass Spectrometer

8.3.1 Ionization Mode: Electron impact (70 eV)

8.3.2 Static Resolution: 1:600 (10% valley) or 1:10,000 depending upon requirements. Usually the sample extracts are initially analyzed using low resolution MS, then if PCDD/PCDF are detected, it is desirable to analyze a second portion of the sample extract using high resolution MS.

8.3.3 Source Temperature: 250°C

8.3.4 Ions Monitored: Computer-Controlled Selected-Ion Monitoring, See Table 1 for list of ion masses monitored and time intervals during which ions characteristic of each class of CDDs and CDFs are monitored.

8.4 Calibration Procedures:

8.4.1 Calibrating the MS Mass Scale: Perfluoro Kerosene, decafluorotriphenyl phosphine, or any other accepted mass marker compound must be introduced into the MS, in order to calibrate the mass scale through at least m/z 500. The procedures specified by the manufacturer for the particular MS instrument used are to be employed for this purpose. The mass calibration should be rechecked at least at 8 hr. operating intervals.

8.4.2 Table 1 shows the GC temperature program typically used to resolve each chlorinated class of PCDD and PCDF from the other chlorinated classes, and indicates the corresponding time intervals during which ions indicative of each chlorinated class are monitored by the MS. This temperature program and ion monitoring time cycle must be established by each analyst for the particular instrumentation used by injecting aliquots of Standard Mixtures C, D. and E (See earlier section of this protocol for description of these mixtures). It may be necessary to adjust the temperature program and ion monitoring cycles slightly based on the observations from analysis of these mixtures.

8.4.3 Checking GC Column Resolution for 2,3,7,8-TCDD and 2,3,7,8-TCDF: Utilize the column-resolution TCDD and TCDF isomer mixtures (Standard Mixtures D and E, containing 50 pg/μl, respectively of the appropriate TCDD and TCDF isomers) to verify that 2,3,7,8-TCDD and 2,3,7,8-TCDF are separated from the other TCDD and TCDF isomers, respectively. A 20% valley or less must be obtained between the mass chromatographic peak observed for 2,3,7,8-TCDD and adjacent peaks arising from other TCDD isomers,and similar separation of 2,3,7,8-TCDF from other neighboring TCDFs,is required. Standard Mixture D is utilized with the DB5 column and Standard Mixture E with the DB-225 column. Analyze the column performance standards using the instrumental parameters specified in Sections 8.2 and 8.3, and in Table 1. The column performance evaluation must be performed each time a new column is installed in the gas chromatograph, and at least once during each 8 hour operating period. Providing that the same column is employed for a

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period of time, its performance can also be gauged by noting the peak width (at 1/2 peak height) for 2,3,7,8-TCDD or for 2,3,7,8-TCDF. If this peak width is observed to broaden by 20% or more as compared to the usual width for satisfactory operation, then the column resolution is suspect and must be checked. If the column resolution is found to be insufficient to resolve 2,3,7,8-TCDD and 2,3,7,8-TCDF from their neighboring TCDD and TCDF isomers, respectively, (as measured on the two different columns used for resolving these two isomers), then a new DB-5 and/or DB-225 GC column must be installed.

8.4.4 Calibration of the GC-MS-DS system to accomplish quantitative analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF, and of the total tetra-through octa-CDDs and CDFs contained in the sample extract, is accomplished by analyzing a series of at least three working calibration standards. Each of these standards is prepared to contain the same concentration of each of the stable-isotopically labelled internal standards used here (Standard Mixture A) but a different concentration of native PCDD/PCDF (Standard Mixture C). Typically, mixtures will be prepared so that the ratio of native PCDD and PCDF to isotopically-labelled PCDD and PCDF will be on the order of 0.1, 0.5 and 1.0 in the three working calibration mixtures. The actual concentrations of both native and isotopically-labelled PCDD and PCDF in the working calibration standards will be selected by the analyst on the basis of the concentrations to be measured in the actual sample extracts. At the time when aliquots of each of the standards are injected (and also when injecting aliquots of actual sample extracts), if desired, an aliquot of a standard containing typically 1 ng of $^{37}Cl_4$-2,3,7,8-TCDD (Standard B) can be drawn into the micro syringe containing the calibration solution described above (or the sample extract) and this is then co-injected along with the sample extract in order to obtain data permitting calculation of the percent recovery of the $^{13}C_{12}$-2,3,7,8-TCDD internal standard. Equations for calculating relative response factors from the calibration data derived from the calibration standard analyses, and for calculating the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD and the other isotopically-labelled PCDD and PCDF, and the concentration of native PCDD and PCDF in the sample (from the extract analysis), are summarized below. In these calculations, as can be seen, 2,3,7,8-TCDD is employed as the illustrative model. However, the calculations for each of the other native dioxins and furans in the sample analyzed are accomplished in an analgous manner. It should be noted that in view of the fact that stable-isotopically labelled internal standards corresponding to each tetra- through octachlorinated class are not used here (owing to limited availability at this time) the following approach is adopted: For quantitation of tetrachlorinated dibenzofurans $^{13}C_{12}$-2,3,7,8-TCDF is used as the internal standard. For quantitation of tetrachloro-dibenzo-p-dioxins, $^{13}C_{12}$-2,3,7,8-TCDD is used as the internal standard. For quantitation of PeCDD, HxCDD, PeCDF, and HxCDF, the corresponding stable-isotopically labelled HxCDD and HxCDF internal standards are used. For quantitation of HpCDD, OCDD, and HpCDF, OCDF, the isotopically-labelled OCDD and OCDF, respectively, are used. Inherent in this approach is the assumption that the response factors for each of the isomers of each chlorinated class are the same, and in the case of the penta- and hepta-CDDs and CDFs, the assumption is made that the responses for these two classes are equivalent to those for the tetra-isomers and the octa-isomers, respectively.

8.4.5 Equations for Calculating Response Factors, Concentration of 2,3,7,8-TCDD In An Unknown Sample, and Recoveries of Internal Standards.

Equation 1: Response Factor (RRF) for native 2,3,7,8-TCDD using $^{13}C_{12}$-2,3,7,8-TCDD as an internal standard.

$$RRF_d = (A_s C_{is} / A_{is} C_s)$$

where: A_s = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

A_{is} = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

C_{is} = Concentration of the internal standard (pg./µL.)

C_s = Concentration of the 2,3,7,8-TCDD (pg./µL.)

Equation 2: Response Factor (RRF) for $^{37}Cl_4$-2,3,7,8-TCDD, the co-injected external standard.

$$RRF_f = (A_{is} C_{es})/(A_{es} C_{is})$$

where: A_{is} = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

A_{es} = SIM response for co-injected $^{37}Cl_4$-2,3,7,8-TCDD external standard at m/z 328 - 0.009 (SIM response for native 2,3,7,8-TCDD at m/z 322)

C_{is} = Concentration of the internal standard (pg./µL.)

C_{es} = Concentration of the external standard (pg./µL.)

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Equation 3: Calculation of concentration of native 2,3,7,8-TCDD using $^{13}C_{12}$-2,3,7,8-TCDD as internal standard

Concentration, pg./g. = $(A_s)\ (I_s)/(A_{is})(RRF_d)(W)$

where: A_s = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

A_{is} = SIM response for the $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

I_s = Amount of internal standard added to each sample (pg.)

W = Weight of soil or waste in grams

RRF_d = Relative response factor from Equation 1

Equation 4: Calculation of % recovery of $^{13}C_{12}$-2,3,7,8-TCDD internal standard

% Recovery = $100(A_{is})(E_s)/(A_{es})(I_i)(RRF_f)$

A_{is} = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

A_{es} = SIM response for $^{37}Cl_4$-2,3,7,8-TCDD external standard ion at m/z 328 - 0.009 (SIM Response for native 2,3,7,8-TCDD at m/z 322)

E_s = Amount of $^{37}Cl_4$-2,3,7,8-TCDD external standard co-injected with sample extract (ng.)

I_i = Theoretical amount of $^{13}C_{12}$-2,3,7,8-TCDD internal standard in injection

RRF_f = Relative response factor from Equation 2

As noted above, procedures similar to these are applied to calculate analytical results for all of the other PCDD/PCDF determined in this method.

8.5 Criteria Which GC-MS Data Must Satisfy for Identification of PCDD/PCDF in Samples Analyzed and Additional Details of Calculation Procedures.

In order to identify specific PCDD/PCDF in samples analyzed, the GC-MS data obtained must satisfy the following criteria:

8.5.1 Mass spectral responses must be observed at both the molecular and fragment ion masses corresponding to the ions indicative of each chlorinated class of PCDD/PCDF identified (see Table 1) and intensities of these ions must maximize essentially simultaneously (within ± 1 second). In addition, the chromatographic retention times observed for each PCDD/PCDF signal must be correct relative to the appropriate stable-isotopically labelled internal standard and must be consistent with the retention time windows established for the chlorinated group to which the particular PCDD/PCDF is assigned.

8.5.2 The ratio of the intensity of the molecular ion $(M)^+$ signal to that of the $(M+2)^+$ signal must be within ± 10% of the theoretically expected ratio (for example, 0.77 in the case of TCDD; therefore the acceptable range for this ratio is 0.62 to 0.92).

8.5.3 The intensities of the ion signals are considered to be detectable if each exceeds the baseline noise by a factor of at least 3:1. The ion intensities are considered to be quantitatively measurable if each ion intensity exceeds the baseline noise by a factor of at least 5:1[c].

8.5.4 For reliable detection and quantitation of PCDF it is also desirable to monitor signals arising from chlorinated diphenyl ethers which, if present could give rise to fragment ions yielding ion masses identical to those monitored as indicators of the PCDF. Accordingly, in Table 1, appropriate chlorinated diphenyl ether masses are specified which must be monitored simultaneously with the PCDF ion-masses. Only when the response for the diphenyl ether ion mass is not detected at the same time as the PCDF ion mass can the signal obtained for an apparent PCDF be considered unique.

8.5.5 Measurement of the concentration of the congeners in a chlorinated class using the methods described herein is based on the assumption that all of the congeners are identical to the calibration standards employed in terms of their respective chemical and separation properties and in terms of their respective gas chromatographic and mass spectrometric responses. Using these assumptions, for example, the $^{13}C_{12}$-2,3,7,8-TCDD internal standard is utilized as the internal calibration standard for all of the 22 TCDD isomers or congeners. Furthermore, the concentration of the total TCDD present in a sample extract is determined by calculating, on the basis of the standard procedure outlined above, the concentration of each TCDD isomer peak (or peaks for multiple TCDD isomers, where these coelute) and these individual concentrations are subsequently summed to obtain the concentration of "total" TCDD.

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[c] In practice, the analyst can estimate the baseline noise by measuring the extension of the baseline immediately prior to each of the two mass chromatographic peaks attributed to a given PCDD or PCDF. Spurious signals may arise either from electronic noise or from other organic compounds in the extract. Since it may be desirable to evaluate the judgement of the analyst in this respect, copies of original mass chromatograms must be included in the report of analytical results.

8.6 Frequently, during the analysis of actual sample extracts, extraneous compounds which are present in the extract (those organic compounds not completely removed during the clean-up phase of the analysis) can cause changes in the liquid and gas chromatographic elution characteristics of the PCDD/PCDF (typically retention times for the PCDD/PCDF are prolonged). Such extraneous organic compounds, when introduced into the mass spectrometer source may also result in a decrease in the sensitivity of the MS because of suppression of ionization, and other affects such as charge transfer phenomena. The shifts in chromatographic retention times are usually general shifts, that is, the relative retention times for the PCDD/PCDF are not changed, although the entire elution time scale is prolonged. The analyst's intervention in the GC-MS operating sequence can correct for the lengthened GC retention times which are sometimes observed due to the presence of extraneous organics in the sample extract. For example, using the program outlined in Table 1, if the retention time observed for 2,3,7,8-TCDD (which normally is 19.5 minutes) is lengthened by 30 seconds or more, appropriate adjustments in the programming sequence outlined in Table 1 can be made, that is, each selected ion-monitoring program is delayed by a length of time proportionate to the lengthening of the retention time for the 2,3,7,8-TCDD isomer. In the case of ionization suppression, this phenomenon is inherently counteracted by the internal standard approach. However, if loss of sensitivity due to ionization suppression is severe, additional clean-up of the sample extract may be required in order to achieve the desired detection limits.

9. Quality Assurance/Quality Control

9.1 Quality assurance and quality control are ensured by the following provisions:

9.1.1 Each sample analyzed is spiked with stable isotopically labelled internal standards, prior to extraction and analysis. Recoveries obtained for each of these standards should typically be in the range from 60-90%. Since these compounds are used as true internal standards however, lower recoveries do not necessarily invalidate the analytical results for native PCDD/PCDF, but may result in higher detection limits than are desired.

9.1.2 Processing and analysis of at least one method blank sample is accomplished for each set of samples (a set being defined as 20 samples or less).

9.1.3 It is desirable to analyze at least one sample spiked with representative native PCDD/PCDF for each set of 20 or fewer samples. The result of this analysis provides an indication of the efficacy of the entire analytical procedure. The results of this analysis will be considered acceptable if the detected concentration of each of the native

PCDD/PCDF added to the sample is within ±50% of the known concentration. (An appropriate set of native isomers to be added here is a set such as that indicated for Standard Mixture C.)

9.1.4 At least one of the samples analyzed out of each set (of 20 samples or less) is analyzed in duplicate and the results of the duplicate analysis are included in the report of data.

9.1.5 Performance evaluation samples prepared by EPA, or other laboratories, which contain representative PCDD/PCDF in concentrations approximating those present in typical field samples being analyzed (but unknown to the analyzing lab) should be periodically distributed to laboratories accomplishing these analyses.

9.1.6 Sources of all calibration and performance standards used in the analyses and the purity of these materials must be specified in the data report.

10. Data Reporting

10.1 Each report of analyses accomplished using the protocol described herein will typically include tables of results which include the following:

10.1.1 Complete identification of the samples analyzed (sample numbers and source).

10.1.2 The dates and times at which all analyses were accomplished. This information should also appear on each mass chromatogram included with the report.

10.1.3 Raw mass chromatographic data which consists of the absolute intensities (based on either peak height or peak area) of the signals observed for the ion-masses monitored (See Table 1).

10.1.4 The calculated ratios of the intensities of the molecular ions for all PCDD/PCDF detected.

10.1.5 The calculated concentrations of native 2,3,7,8-TCDD and 2,3,7,8-TCDF, and the total concentrations of the congeners of each class of PCDD/PCDF for each sample analyzed, expressed in nanograms TCDD per gram of sample (that is, parts-per-billion) as determined from the raw data. If no PCDD/PCDF are detected, the notation "Not Detected" or "N.D." is used, and the minimum detectable concentrations

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(or detection limits) are reported.

10.1.6 The same raw and calculated data which are provided for the actual samples will also be reported for the duplicate analyses, the method blank analyses, the spiked sample analyses and any other QA or performance samples analyzed in conjunction with the actual sample set(s).

10.1.7 The recoveries of the internal standards in percent.

10.1.8 The recoveries of the native PCDD/PCDF from spiked samples in percent.

10.1.9 The calibration data, including response factors calculated from the three point calibration procedure described elsewhere in this protocol. Data showing that these factors have been verified at least once during each 8 hour period of operation or with each separate set of samples analyzed must be included.

10.1.10 The weight or quantity of the original sample analyzed.

10.1.11 Documentation of the source of all PCDD/PCDF standards used and available specifications on purity.

10.1.12 In addition to the tables described above, each report of analyses will include all mass chromatograms obtained for all samples analyzed, as well as for all calibration, GC column performance, and GC "window" definition runs and results of column performance checks.

10.1.13 Any deviations from the procedures described in this protocal which are applied in the analyses of samples will be documented in detail in the analytical report.

11. Typical Data Indicative of Method Performance - Precision and Accuracy.

11.1 The method described herein has typically been employed to quantitatively determine 2,3,7,8-TCDD in combustion product samples at concentrations as low as 10 picograms/gram and as high at 100 μg/g. Concentrations of the other PCDD/PCDF which can be detected typically fall within the range of 20 picograms/isomer/gram of sample, to 100 picograms/g of sample. Of course, the limits of detection which can be practically achieved are dependent on the quantity of sample available

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and the amount and kind of other interferring organic residues which are present in the sample. With respect to precision, the average deviation of data obtained from the analyses of a number of aliquots of the same sample containing the 2,3,7,8-TCDD isomer in the 250-300 ppb range is estimated to be ±10% or better. Data on the precision of quantitation of multiple PCDD/PCDF in a single sample are not as yet available. As yet, there is inadequate interlaboratory and performance evaluation data available to specify the accuracy which can be expected of the analytical procedures described herein.

TABLE 1. Sequence of Operations in GC-MS-DS Quantitation of CDDs/CDFs in Extracts of Environmental Samples

Elapsed Time (min)	Event	GC Column Temperature* (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of $[M]^+:[M+2]^+$
0.00	Injection, splitless	190					
1.00	Turn on split valve	190					
1.00	Begin temp. program to 220°C	190	5				
6.00	Open column flow to mass spectrometer	215	5				
7.00	Column temperature hold	220					
14.00	Start Tetra Program; sweep = 350 ppm; time/mass = 0.08 sec.			240.938	$[M-COCl]^+$	TCDF	
				258.930	$[M-COCl]^+$	TCDD	
				303.902	$[M]^+$	TCDF	0.77
				305.899	$[M+2]^+$	TCDF	
				315.942	$[M]^+$	$^{13}C_{12}$-TCDF	
				319.897	$[M]^+$	TCDD	0.77
				321.894	$[M+2]^+$	TCDD	
				327.885	$[M]^+$	$^{37}Cl_4$-TCDD	
				331.937	$[M]^+$	$^{13}C_{12}$-TCDD	
				373.840	$[M]^+$	HxDPE^a.	
22.00	Stop Tetra Program	220					
22.50	Start Penta Program; sweep = 350 ppm; time/mass = 0.12 sec.			274.899	$[M-COCl]^+$	PeCDF	
				290.894	$[M-COCl]^+$	PeCDD	
				337.863	$[M]^+$	PeCDF	0.61
				339.860	$[M+2]^+$	PeCDF	
23.00	Begin temp. program to 235°	220	5	353.858	$[M]^+$	PeCDD	0.61
26.00	Column temperature hold	235		355.855	$[M+2]^+$	PeCDD	
				407.801	$[M]^+$	HpDPE^a.	
32.00	Stop Penta Program						
32.50	Start Hexa Program; sweep = 350 ppm; time/mass = 0.20 sec.	235		310.857	$[M-COCl]^+$	HxCDF	
				326.852	$[M-COCl]^+$	HxCDD	
				373.821	$[M]^+$	HxCDF	1.23
				375.821	$[M+2]^+$	HxCDF	
				385.861	$[M]^+$	$^{13}C_{12}$-HxCDF	
				389.816	$[M]^+$	HxCDD	1.23
				391.813	$[M+2]^+$	HxCDD	
				411.856	$[M]^+$	$^{13}C_{12}$-HxCDD	
				443.759	$[M]^+$	ODPE^a.	

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TABLE 1. Sequence of Operations in GC-MS-DS Quantitation of CDDs/CDFs in Extracts of Environmental Samples (Cont.)

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of $[M]^+:[M+2]^+$
33.00	Begin temp. program to 250°C	235	5				
36.00	Column temperature hold	250					
42.50	Stop Hexa Program						
43.00	Start Hepta Program; sweep = 350 ppm; time/mass = 0.30 sec.	250		344.818	$[M-COCl]^+$	HpCDF	
				360.813	$[M-COCl]^+$	HpCDD	
				407.782	$[M]^+$	HpCDF	1.03
				409.779	$[M+2]^+$	HpCDF	
				423.777	$[M]^+$	HpCDD	1.03
				425.774	$[M+2]^+$	HpCDD	
				477.720	$[M^+]$	NDPE[a].	
53.00	Stop Hepta Program	250					
53.50	Start Octa Program; sweep = 350 ppm; time/mass = 0.30 sec.	250		378.768	$[M-COCl]^+$	OCDF	
				394.774	$[M-COCl]^+$	OCDD	
54.00	Begin temp. program to 270°	250°	5	441.732	$[M]^+$	OCDF	0.88
58.00	Column temperature hold	270°		443.740	$[M+2]^+$	OCDF	
				453.772	$[M]^+$	$^{13}C_{12}$-OCDF	
				457.738	$[M]^+$	OCDD	0.88
				459.735	$[M+2]^+$	OCDD	
				469.779	$[M]^+$	$^{13}C_{12}$-OCDD	
				471.776	$[M+2]^+$	$^{13}C_{12}$-OCDD	
				511.681	$[M]^+$	DDPE[a].	
65.00	Stop Octa Program						
65.00	Begin temp. program to 300°	270°	5				
71.00	Column temperature hold	300°					
75.00	Cool Column to 190°						

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[a] HxDFE, HpDPE, ODPE, NDPE, DDPE are abbreviations which designate (respectively) hexachloro-, heptachloro-, octachloro-, nonachloro-, and decachlorodiphenyl ethers.

*The parameters given here are applicable for a 60-meter fused silica capillary GC column coated with DB-5.

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APPENDIX

RECOMMENDED SAFETY AND HANDLING PROCEDURES FOR LABORATORIES CONDUCTING PCDD/PCDF ANALYSES

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Recommended Safety and Handling Procedures in Connection with Implementing the Analytical Protocal for Determination of PCDD/PCDF in Combustion Products

1. The human toxicology of PCDD/PCDF is not well defined at present, although the 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in the course of laboratory animal studies. The 2,3,7,8-TCDD is a solid at room temperature, and has a relatively low vapor pressure. The solubility of this compound in water is only about 200 parts-per-trillion, but the solubility in various organic solvents ranges from about 0.001% to 0.14%. The physical properties of the 135 other tetra-through octachlorinaed PCDD/PCDF have not been well established, although it is presumed that the physical properties of these congeners are generally similar to those of the 2,3,7,8-TCDD isomer. On the basis of the available toxicological and physical property data for TCDD, this compound, as well as the other PCDD and PCDF, should be handled only by highly trained personnel who are thoroughly versed in the appropriate procedures, and who understand the associated risks.

2. PCDD/PCDF and samples containing these are handled using essentially the same techniques as those employed in handling radioactive or infectious materials. Well-ventilated, controlled-access laboratories are required, and laboratory personnel entering these laboratories should wear appropriate safety clothing, including disposable coveralls, shoe covers, gloves, and face and head masks. During analytical operations which may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn at all times while working in the analytical laboratory with PCDD/PCDF. Various types of gloves can be used by personnel, depending upon the analytical operation being accomplished. Latex gloves are generally utilized, and when handling samples thought to be particularly hazardous, an additional set of gloves are also worn beneath the latex gloves (for example, Playtex gloves supplied by American Scientific Products, Cat. No. 67216). Bench-tops and other work surfaces in the laboratory should be covered with plastic-backed absorbent paper during all analytical processing. When finely divided samples (dusts, soils, dry chemicals) are being processed, removal of these from sample containers, as well as other operations, including weighing, transferring, and mixing with solvents, should all be accomplished within a glove box. Glove boxes, hoods and the effluents from mechanical vacuum pumps and gas chromatographs on the mass spectrometers should be vented to the atmosphere preferably only after passing through HEPA particulate filters and vapor-sorbing charcoal.

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3. All laboratory ware, safety clothing and other items potentially contaminated with PCDD/PCDF in the course of analyses must be carefully secured and subjected to proper disposal. When feasible, liquid wastes

are concentrated, and the residues are placed in approved steel hazardous waste drums fitted with heavy gauge polyethylene liners. Glass and combustible items are compacted using a dedicated trash compactor used only for hazardous waste materials and then placed in the same type of disposal drum. Disposal of accumulated wastes is periodically accomplished by high temperature incineration at EPA-approved facilities.

4. Surfaces of laboratory benches, apparatus and other appropriate areas should be periodically subjected to surface wipe tests using solvent-wetted filter paper which is then analyzed to check for PCDD/PCDF contamination in the laboratory. Typically, if the detectable level of TCDD or TCDF from such a test is greater than 50ng/m^2, this indicates the need for decontamination of the laboratory. A typical action limit in terms of surface contamination of the other PCDD/PCDF (summed) is 500ng/m^2. In the event of a spill within the laboratory, absorbent paper is used to wipe up the spilled material and this is then placed into a hazardous waste drum. The contaminated surface is subsequently cleaned thoroughly by washing with appropriate solvents (methylene chloride followed by methanol) and laboratory detergents. This is repeated until wipe tests indicate that the levels of surface contamination are below the limits cited.

5. In the unlikely event that analytical personnel experience skin contact with PCDD/PCDF or samples containing these, the contaminated skin area should immediately be thoroughly scrubbed using mild soap and water. Personnel involved in any such accident should subsequently be taken to the nearest medical facility, preferably a facility whose staff is knowledgable in the toxicology of chlorinated hydrocarbons. Again, disposal of contaminated clothing is accomplished by placing it in hazardous waste drums.

6. It is desirable that personnel working in laboratories where PCDD/PCDF are handled be given periodic physical examinations (at least yearly). Such examinations should include specialized tests, such as those for urinary porphyrins and for certain blood parameters which, based upon published clinical observations, are appropriate for persons who may be exposed to PCDD/PCDF. Periodic facial photographs to document the onset of dermatologic problems are also advisable.